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# HANDBOOK OF METALLURGY



# HANDBOOK OF METALLURGY

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ZINC—CADMIUM—MERCURY—BISMUTH—TIN—ANTIMONY  
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# METALLURGY

## ZINC

### PHYSICAL PROPERTIES

ZINC possesses a white colour with a bluish grey tinge, and a high lustre on the freshly fractured surface. It crystallises in the cubical system. The nature of the fracture depends upon the temperature at which the metal is poured, and is independent of the subsequent rate of cooling; it is coarsely lamellar when the fluid metal is heated to redness before pouring, but fine grained when it is cast at its melting point. When heated to  $160^{\circ}$  C. and bent, it gives out a "cry" like tin, but feebler.

The specific gravity of unrolled zinc is 6.861 according to Brisson, 6.9154 according to Karsten, 7.149 according to Matthiessen. Zinc cast at its melting point and slowly cooled has a specific gravity of 7.145 according to Bolley, and of 7.128 according to Rammelsberg; whilst when cast at a red heat and cooled slowly, it is 7.120 according to the former, and 7.101 according to the latter observer; if cast at its melting point and cooled rapidly, it has, according to the former, a specific gravity of 7.158, and, according to the latter, of 7.147; whilst the respective results obtained from zinc, poured at a red heat and cooled rapidly, are 7.109 and 7.037.<sup>1</sup> Its specific gravity is raised from 7.2 to 7.3 by rolling.

At the ordinary temperature, zinc is so brittle that ingots and slabs are readily broken; between  $100^{\circ}$  and  $150^{\circ}$  C. it becomes so malleable that it can be rolled into thin sheets and drawn into wire; at  $205^{\circ}$  C. it again becomes so brittle that it can be pounded into powder. When cast at a temperature near to its melting point, zinc is more extensible than when cast at a higher temperature. In

<sup>1</sup> Stölzell, *Metallurgie*, Brunswick, 1874, p. 752.

hardness, zinc lies between copper and tin, or more accurately between silver and platinum.

According to Karmarsch the tenacity of cast zinc is 197·5 kilos. and that of sheets and wire between 1315 and 1560 kilos. per square centimetre (2,809 lbs., 18,703 lbs. and 22,188 lbs. per square inch respectively). According to Wertheim the values are 1·5 and 1250 kilos. respectively for cast zinc rod and for drawn wire of 1 mm. diameter.

According to Regnault, the specific heat of zinc is 0·09555 for temperatures between 0° and 100° C. Other investigators give 0·0927 between 0° and 100° C. and 0·1015 between 100° and 300° C.

Zinc expands by  $\frac{1}{310}$  of its length when heated from 0° to 100° C. According to Calvert and Johnson, the coefficient of linear expansion of hammered zinc is 0·002193.

The thermal conductivity of zinc, silver being taken at 100, is 19 according to Wiedemann and Franz; that of cast zinc is between 60·8 and 62·8, and that of rolled zinc 64·1, according to Calvert and Johnson.

The electric conductivity of zinc, silver being taken at 100, is 24·06 according to Becquerell, 27·39 according to Matthiessen, and 29·90 according to Weiller.<sup>1</sup>

The melting point of zinc is variously given at 412° by Daniell, 415° by Roberts-Austen, 419° by Haycock and Neville, and 434° by Person. It volatilises at bright redness, its boiling point being 891° C. according to Becquerell; Deville and Troost give 1040° C., Violle 929·6° C., Roberts-Austen 940° C., Thum 1000° C., Komorek 1050° C., and Berthelot 913—927° C. (*Compt. rend.*, CXXXI. vi. 380—382). According to Barus the boiling point rises by 1·5° C. for every increase in pressure of one centimetre of mercury above the atmospheric pressure (76 cm.). Silver (melting about 954° C.) does not melt in zinc vapour. Zinc vapour can be condensed to fluid zinc by cooling; the more diluted it is with air, the more difficult is this vapour to condense. When the temperature of the vapour falls below the melting point of zinc, it solidifies in the form of powder, forming what is known as *zinc fume*. According to Lynen,<sup>2</sup> the zinc vapour produced in the extraction of zinc from its ores condenses between 415° and 550° C. According to Hempel,<sup>3</sup> zinc vapour, formed by the reduction of zinc white in the blast furnace, was not condensed from the gases accompanying it until the temperature had fallen below 470°.

<sup>1</sup> *Journ. Franklin Inst.* April, 1892, p. 263.

<sup>2</sup> *Zinc distillation furnace with common condensing chamber*, London, 1893.

<sup>3</sup> *Berg- und Hüttenm. Ztg.* 1893, No. 41, 42.

When heated in the air to  $500^{\circ}$  C. (or  $505^{\circ}$  C., according to Daniell), zinc burns with bright greenish and bluish white flame to zinc oxide. In a finely divided condition it is sometimes kindled spontaneously by rapid oxidation.

Commercial zinc is generally rendered impure by the presence of lead, cadmium and iron, and in many cases also of small quantities of tin, copper, arsenic, antimony, silicon, sulphur, carbon and chlorine. The presence of thallium, indium and gallium has also been detected in commercial zinc.

The effect of the impurities contained in the zinc upon the properties of the latter has been investigated by Karsten<sup>1</sup> and by Eliot and Storer.<sup>2</sup>

*Lead* is present in most varieties of commercial zinc. Karsten found the proportion in Silesian zinc to vary between 0.24 and 2.36 per cent. Eliot and Storer found only 0.079 per cent. of lead in New Jersey zinc, and none at all in zinc from Pennsylvania reduced from the silicate.

The amount of lead that zinc can take up varies with the temperature, being greater the higher the temperature. According to the most recent researches of Roessler and Edelmann on this subject, zinc takes up 1.7 per cent. of lead at its melting point and 5.6 per cent. at  $650^{\circ}$  C. Romanoff and Spring state that zinc takes up 25.5 and 7 per cent. of lead at  $900^{\circ}$  and  $650^{\circ}$  C. respectively. If more lead is present than corresponds to the temperature of the metal, the excess separates out in the liquid state.

A considerable proportion of lead makes zinc tender; with  $1\frac{1}{2}$  per cent. of lead, it can still be rolled without cracking, but becomes softer and more tender. It can even be rolled with 3 per cent. of lead, but shows the above characteristics more markedly. Before zinc is rolled, lead is removed from it as completely as possible by remelting the metal and allowing it to settle. Lead in quantity has a bad effect also on the properties of brass.

*Cadmium* occurs in most varieties of zinc, because this metal is present in most zinc ores. As cadmium is considerably more volatile than zinc, it is only to be found in very small amounts in commercial zinc. According to some experiments of Mentzel in 1829, at the Lydognia Works in Upper Silesia, cadmium would seem to diminish the softness of zinc as soon as it is present in certain

<sup>1</sup> Karsten's *Archiv*, 1842, vol. xvi. p. 597.

<sup>2</sup> "On the impurities of commercial zinc with reference to the residue insoluble in dilute acid, to sulphur and to arsenic." *Memoirs Am. Acad. Arts and Sciences*, new series, vol. viii. 1860.

proportions. In the small amounts in which it exists in commercial zinc, it has no injurious effects upon the properties of the latter.

*Iron* may be contained in zinc to the extent of several per cent. but rarely exceeds 0·2 per cent. The highest proportion of iron found by Karsten was 0·24 per cent., and by Percy<sup>1</sup> 1·4 per cent. Eliot and Storer found 0·21 per cent. of iron in New Jersey zinc, and 0·05 to 0·07 per cent. in sheet zinc from Berlin. Oudemans found in a difficultly fusible substance with white, lustrous, hackly fracture, which collected in iron kettles in which zinc had been kept molten for many weeks, 4·6 per cent. of iron. Zinc obtained from flue dust (containing 22 per cent. of zinc) from the blast furnaces in Upper Silesia was found by Karsten to contain 0·71 per cent. of iron. The hard zinc got in the refining of zinc contains also large amounts of iron. In small quantities—up to 0·2 per cent. according to Karsten—iron does not affect the properties of zinc; in larger proportion, however, it renders the zinc hard and unfit for rolling.

*Tin* has been found by Eliot and Storer in American zinc from New Jersey and in English zinc made by Vivian and Co., of Swansea. A sample of zinc from Freiberg contained 0·07 per cent. of tin. According to Karsten, 1 per cent. of tin renders zinc brittle at those temperatures at which it would otherwise be malleable.

*Copper* was found by Eliot and Storer in New Jersey zinc. Zinc from Missouri was found to contain 0·0013 to 1·1123 per cent. of copper, and 0·0002 per cent. was found in zinc from Upper Silesia. Karsten found that  $\frac{1}{2}$  per cent. of copper makes zinc harder and brittle—so much so that it showed ragged edges on rolling, and could not be rolled without cracking.

*Arsenic* occurs in small quantities in many varieties of zinc. Missouri zinc contained 0·0603 per cent. Considerable quantities of arsenic are said to make zinc brittle, and antimony has a similar action, though there is no particular information on this point.

*Sulphur* could not be detected by Karsten in any of the numerous samples of zinc examined by him. On the other hand, Eliot and Storer, as also Alfred Taylor, found small amounts of sulphur (up to 0·0741 per cent.) in a large number of varieties of zinc. According to Funk<sup>2</sup> the sulphur is present in the form of sublimed zinc sulphide. No investigations have been made as to the effect of sulphur on the properties of zinc; the small amounts found in zinc seem not to affect the latter.

*Carbon* has been found by Funk to the extent of 0·1775 per cent.

<sup>1</sup> *Metallurgy. First Division*, 1861, p. 590.

<sup>2</sup> *Zeit. anorg. Chem.* 1896, p. 49.



Funk regards it as mechanically mixed, not combined with the zinc. Rodwell<sup>1</sup> found sulphate of lead, carbon and a trace of iron in the black residue that remains when commercial zinc is dissolved in sulphuric acid. Such a small proportion of carbon seems not to affect the zinc in the least. Nothing is known as to its action in larger quantities.

*Chlorine* has been detected by C. Künzel in the Belgian zinc that was prepared from the dross of galvanised iron, in quantities of 0·2 to 0·3 per cent.; this zinc, which contained only traces of lead and iron, could not be rolled.

*Silicon* has been found in Missouri zinc in quantities up to 0·1374 per cent. Its influence on the properties of the metal has not been investigated.

### CHEMICAL PROPERTIES

Zinc is not affected in dry air at ordinary temperatures; in damp air in the presence of carbon dioxide, it becomes coated with a layer of hydrated basic zinc carbonate, which layer is sufficiently dense to protect the metal beneath it from any further atmospheric action.

The massive metal is not attacked at ordinary temperatures by water free from air, but in the presence of air and carbon dioxide it is changed into the above-named basic carbonate. Pure compact zinc is not affected by cold or boiling pure water; commercial zinc is, however, superficially oxidised, hydrogen being evolved. The film of oxide thus formed shields the metal from the further action of water.

When zinc is heated in the air, it takes fire at a temperature approaching redness (at 505° C. according to Daniell), and burns with a luminous greenish and bluish white flame to zinc oxide, which in part floats as an incrustation upon the surface of the molten metal, and in part appears as a snow-white flocculent body (*lana philosophica*).

Zinc decomposes water at a red heat, and is transformed into zinc oxide with the evolution of hydrogen. Zinc in a very fine state of division exerts a very feeble decomposing action upon water even at ordinary temperatures; this action is favoured by the presence of acids and alkalies.

Zinc is soluble in most acids. In dilute sulphuric and hydrochloric acids it dissolves with the evolution of hydrogen. According to Bolley, zinc melted at a low temperature dissolves more slowly than when melted at a red heat.

<sup>1</sup> *Chem. News*, January, 1861. No. 57.

Chemically pure zinc dissolves readily in nitric acid, though it is but slightly attacked by other acids, weak or strong. The cause of this is, according to Werren,<sup>1</sup> that the metal becomes surrounded by a film of hydrogen the moment it is dipped into the acid; on boiling, this film is torn, and the zinc dissolves. Zinc dissolves readily in cold nitric acid, because the latter oxidises the hydrogen evolved. The solubility of zinc in sulphuric acid is promoted by the addition of chromic acid and of hydrogen peroxide. Impure zinc dissolves readily in acids, because the hydrogen is evolved, not from the zinc, but from the more electronegative foreign metals.

Zinc is converted by carbon dioxide into zinc oxide at a red heat, carbon monoxide being formed.

Aqueous solutions of the alkalies attack zinc with the evolution of hydrogen, but much more slowly than do acids. The action is more energetic when the zinc is in contact with iron or platinum so as to form a galvanic couple. Zinc is thus easily dissolved in potash lye when contained in an iron vessel.

Zinc precipitates all the malleable heavy metals except iron and nickel from their solutions in the metallic state. Conversely it is not precipitated as metal from its solutions by any heavy metal nor even by aluminium.

Sulphur combines with zinc at a red heat, producing zinc sulphide; the combination is, however, imperfect, because the zinc, even when in fine powder and intimately mixed with powdered sulphur, is protected by the superficial layer of the infusible sulphide thus formed. Zinc can be converted completely into sulphide by rapid heating with cinnabar, as also by fusion with potassium sulphide.

By fusion with litharge, zinc is converted into oxide, whilst the oxide of lead is reduced to metal.

By fusion with alkaline carbonates, zinc is converted into oxide with the evolution of carbon monoxide. When it is similarly treated with alkaline sulphates, zinc sulphate and zinc oxide are formed, sulphur dioxide being evolved. Zinc unites with phosphorus at a red heat in various proportions to form phosphides of zinc.

Zinc unites with arsenic in all proportions at a moderate temperature, alloys of the two metals being produced. The more arsenic it contains, the less fusible does the zinc become; alloys containing large proportions of arsenic are absolutely infusible.

Zinc forms alloys with a large number of metals, *e.g.* aluminium, antimony, bismuth, gold, iron, lead, mercury, silver and tin.

<sup>1</sup> *Ber. deut. Chem. Ges.* 1891, 24, p. 1785.

*Aluminium* alloys with zinc in all proportions. More than 3 per cent. of zinc makes these alloys brittle.<sup>1</sup>

*Antimony* forms brittle alloys with all proportions of zinc.

*Bismuth* and zinc alloy on melting, two layers being formed on cooling. The upper layer contains 97·6 per cent. of zinc and 2·4 per cent. of bismuth, and the lower layer 85·7 to 91·4 per cent. of bismuth and 14·3 to 8·6 per cent. of zinc.

*Copper* alloys in all proportions with zinc, the brasses being the alloys of practical importance. With the rise in the proportion of copper (up to 85 per cent.) the ductility increases.

*Gold and Zinc* form alloys in all proportions.

*Iron* gives a hard brittle alloy.

*Lead* melted with zinc forms on cooling two alloys with preponderance of each metal respectively. Commercial zinc is usually a zinc-lead alloy containing 1 per cent. of lead.

*Quicksilver* forms a white brittle amalgam readily with zinc. Excess of quicksilver renders this amalgam viscous.

*Silver* combines with zinc readily at high temperatures, less readily at lower temperatures.

*Tin* alloys with zinc in all proportions.

Other alloys are formed with magnesium, nickel, cobalt, tellurium and sodium, and a long series is known containing zinc and two other metals.

## CHEMICAL REACTIONS OF ZINC COMPOUNDS THAT ARE OF IMPORTANCE IN THE EXTRACTION OF THE METAL

### ZINC OXIDE ( $\text{ZnO}$ )

Zinc forms only one compound with oxygen, namely, zinc oxide; this occurs in nature as zincite. Recent investigations, however, tend to show that other oxides may exist. Artificially it is prepared by burning zinc, by heating finely divided zinc with nitre, potassium chlorate or arsenic acid, by igniting zinc carbonate, hydrate, sulphate or nitrate, and by the oxidising roasting of zinc sulphide.

It forms a white or pale yellow powder, which becomes lemon-yellow on heating, but regains its white colour on cooling.

Zinc oxide is infusible by itself, and is unaffected at temperatures that are not excessive, but is volatile at a strong white heat. According to the experiments of Stahlschmidt,<sup>2</sup> pure zinc oxide is

<sup>1</sup> *Aluminium*, Richards, London, 1896.

<sup>2</sup> *Berg- und Hüttenm. Ztg.* 1875, p. 69.

perceptibly volatile even at the melting point of silver ( $970^{\circ}\text{C.}$ ); at the melting point of copper ( $1054^{\circ}\text{C.}$ ) its volatility is more marked (15 per cent.). At a white heat it volatilises rapidly. The oxide produced by roasting zinc blende is not volatile at the melting point of silver, though it is considerably so at the melting point of copper.

Zinc oxide is insoluble in pure water. Acids dissolve it readily, as also do solutions of caustic potash and soda, ammonia and ammonium carbonate. With sulphurous acid it forms zinc sulphite.

Although zinc oxide is a strong base, it nevertheless combines also with other bases (with the alkalies, alkaline earths, and with alumina). It does not combine with water to form zinc hydroxide ( $\text{ZnO}\cdot\text{H}_2\text{O}$  or  $\text{Zn}(\text{OH})_2$ ), but this body can be obtained as a white amorphous precipitate by the action of sodium, potassium, calcium or magnesium hydroxides on solutions of zinc salts. Excess of potassium or sodium hydroxides dissolves zinc hydroxide. On heating, zinc hydroxide loses water and forms the oxide.

It is reduced to metal by carbon and carbon monoxide at a bright red heat. According to Hempel's<sup>1</sup> experiments, reduction commences at a temperature below the boiling point of zinc, and is complete at a temperature above it, between bright redness and a white heat.

The researches of Schüpphaus and Lungurtz<sup>2</sup> have shown that the reduction of zinc oxide begins at  $910^{\circ}\text{C.}$ , that is  $10^{\circ}$  below the boiling point of zinc, and is completed at  $1300^{\circ}\text{C.}$  O. Boudouard's<sup>3</sup> experiments point to  $1125^{\circ}$  to  $1150^{\circ}\text{C.}$  as the temperature interval of reduction.

Zinc oxide prepared by precipitation is finer in structure and more easily reduced than the oxide prepared by calcining or roasting the ores. Generally speaking, the oxide produced by the dead-roasting of zinc blende is harder to reduce than that made by calcination of calamine.

When reduced by means of carbon, carbon monoxide is formed: when reduced by carbon monoxide, carbon dioxide is evolved. The former gas is without action on zinc at any temperature, the latter oxidises it at a red heat. The quantity of zinc oxidised in any given case by a mixture of carbon monoxide and dioxide would seem to depend on the one hand upon the ratio in which these gases are present, and on the other hand upon the temperature. (See the reduction of zinc oxide by hydrogen.)

<sup>1</sup> *Berg- und Hüttenm. Ztg.* 1893, Nos. 41 and 42.

<sup>2</sup> *Journ. Soc. Chem. Ind.* Nov. 30, 1899, p. 987.

<sup>3</sup> "Recherches sur les équilibres chimiques," *Ann. Chem. Phys.* vol. 24, p. 74 (1901).

When zinc oxide is heated with a sufficient quantity of carbon to its reducing point, zinc is first reduced by the carbon. The carbon monoxide thus formed itself reduces the oxide of zinc, becoming thereby converted into carbon dioxide. The latter has no opportunity of oxidising the zinc, because it is straightway reduced to carbon monoxide again by the red-hot carbon. As long, therefore, as a sufficiency of red-hot carbon is present, zinc and carbon monoxide alone are produced. Any small amount of oxide produced by the oxidation of zinc is reduced again to metal by the carbon and carbon monoxide. These reactions would seem also to take place in the production of zinc from zinc oxide on the large scale. As carbon monoxide thus acts as a reducing agent, a very intimate mixture of zinc oxide with the carbon, or a very fine state of division of these bodies, is unnecessary.

According to Boudouard (*op. cit.*) the gases evolved on reduction of zinc oxide with carbon contain 99 per cent. of carbon monoxide and 1 per cent. of carbon dioxide.

Hydrogen reduces zinc oxide to zinc at a red heat; the water vapour thus produced oxidises the zinc again to a greater or less extent. According to the experiments of Deville<sup>1</sup> and Dick,<sup>2</sup> zinc chiefly is obtained when a considerable quantity of hydrogen is passed in a rapid stream over the red-hot oxide, whilst almost all the zinc is again oxidised when a slow current of hydrogen is passed over the oxide. The oxidising action of the water vapour upon the zinc would seem to depend both on the ratio of the water vapour to the hydrogen and on the temperature. Deville is of the opinion that the temperature is the essential factor, a rapid current of hydrogen causing a fall in temperature that is not produced by a slow one; at this lower temperature water vapour cannot exert the oxidising action that it does at the higher. Further experiments are needed to decide whether this view is or is not the correct one.

Sulphur attacks zinc oxide when heated, zinc sulphide and sulphur dioxide being produced.

At high temperatures iron<sup>3</sup> reduces zinc oxide to metal.

Zinc oxide unites with silica at a white heat to form silicates. Percy<sup>4</sup> found that the bisilicate could not be made to fuse at the highest white heat, whilst the monosilicates and the lower silicates fused at this temperature to more or less translucent slags of whitish-to greenish-yellow colour. The silicate of zinc which occurs naturally melts at this temperature to an opaque stone-like mass of

<sup>1</sup> *Ann. Chim. Phys.* (3) vol. xliii. p. 479.

<sup>2</sup> Percy, *op. cit.* p. 535.

<sup>3</sup> Percy, *op. cit.* p. 536.

<sup>4</sup> Percy, *op. cit.* p. 536.

greyish-green colour. According to Stelzner and Schulze,<sup>1</sup> incrustations of silicates of zinc often form on the exterior of zinc-distillation muffles, which are permeated by zinc vapours. In one case, these silicates contained:  $\text{ZnO}$ , 56.11 per cent.;  $\text{Fe}_2\text{O}_3$ , 0.81 per cent.;  $\text{SiO}_2$ , 42.77 per cent. These observers found in the blue portions of the muffle walls a zinc-alumina spinel, tridymite, and a glass consisting of silicate of zinc.

Zinc oxide combines with alumina at high temperatures to form aluminates. By heating an intimate mixture of zinc oxide and anhydrous alumina in the equivalent proportions of 1:6, Percy<sup>2</sup> obtained a grey sintered stony mass that scratched flint glass. In the blue portions of the walls of vessels used for distilling zinc, Wohlfahrt, Stelzner and Schulze<sup>3</sup> found a blue zinc-alumina spinel, in which a small portion of zinc oxide was replaced by ferrous oxide, its formula being  $\text{ZnO}, \text{Al}_2\text{O}_3$ , and its composition:—

$\text{ZnO}$ . . . . .	42.60
$\text{FeO}$ . . . . .	1.12
$\text{Al}_2\text{O}_3$ . . . . .	55.61
	<hr/>
	99.33

Zinc aluminate is found in nature as the mineral gahnite. Oxides of iron and zinc combine to form a ferrate of zinc ( $\text{ZnO}.\text{Fe}_2\text{O}_3$  or  $\text{ZnFe}_2\text{O}_4$ ). This body is formed to some extent on heating together the two oxides to redness, and is thus a possible product of the roasting of blende containing iron.

When heated with eight times its weight of oxide of lead, zinc oxide melts to a limpid pale yellow fluid;<sup>4</sup> when from six to seven times its weight is taken, the mass becomes pasty; on further diminishing the proportion of oxide of lead, the mixture becomes difficultly fusible and ultimately infusible.

The behaviour of zinc sulphide with zinc oxide will be found under Zinc Sulphide.

Zinc oxide melts with fixed alkaline carbonates to fluid, colourless transparent substances as long as its weight does not exceed one-fifth of the whole.<sup>5</sup>

Zinc oxide is dissolved as chloride of zinc by a solution of ferric chloride, an equivalent quantity of iron being precipitated as

<sup>1</sup> *Jahrb. f. Berg- u. Hüttenwesen im Königreich Sachsen*, 1881. *Berg- und Hüttenm. Ztg.* 1886, p. 150.

<sup>2</sup> *Op. cit.* p. 539.

<sup>4</sup> Berthier, vol. i. p. 515.

<sup>3</sup> *Loc. cit.*

<sup>5</sup> Berthier, vol. ii. p. 567.

hydroxide. Ferric sulphate in like manner forms zinc sulphate with precipitation of ferric hydroxide.

### ZINC SULPHIDE (ZnS)

Zinc sulphide occurs in nature as zinc blende. This compound can be produced artificially in both the wet and the dry way. In the latter it is obtained by heating zinc oxide with sulphur, or in a stream of sulphuretted hydrogen, by heating zinc filings with cinnabar, by heating zinc filings or granulated zinc with alkaline polysulphides, and by heating zinc sulphate and carbon to a white heat. As already stated, it is only partially formed when zinc and sulphur are heated together, but has been produced by repeated compression of a mixture of these two substances.

In the wet way it is produced as an amorphous white powder by precipitating zinc solutions with ammonium sulphide or sulphuretted hydrogen.

Sulphide of zinc is infusible; according to experiments of Percy<sup>1</sup> it seems to be perceptibly volatile at high temperatures.

It can be melted to a certain extent with other metallic sulphides, forming a regulus, which it tends to render difficultly fusible. It also melts to some extent with slags, decreasing their fusibility unless considerable quantities of ferrous oxide are present in them.

Zinc sulphide is not decomposed by heating (even in the electric furnace<sup>2</sup>) out of contact with air.

When pulverulent zinc sulphide is heated to redness in the air, zinc oxide and sulphate are formed, sulphur dioxide being given off. When the temperature rises to cherry redness, zinc sulphate is decomposed into sulphur trioxide, sulphur dioxide, oxygen and basic zinc sulphate; when it rises still further to a full red heat approaching whiteness, the last-named salt is decomposed into zinc oxide, sulphur trioxide, sulphur dioxide and oxygen.

When zinc sulphide is heated in water vapour, zinc oxide and sulphuretted hydrogen are formed; this decomposition is, however, imperfect, and requires a temperature up to white heat.

When zinc sulphide is heated with carbon or in carbon-lined crucibles it volatilises completely according to Percy,<sup>3</sup> or only leaves behind, if it contains iron, a residue of ferrous sulphide free from zinc. It is not stated whether the zinc sulphide volatilised unchanged or whether it was reduced by the carbon (with the formation

<sup>1</sup> Op. cit. p. 540.

<sup>2</sup> Mourlot, *Compt. rendus*, 124, I. 768 (1897).

<sup>3</sup> Op. cit. p. 543.

of carbon disulphide), in which case metallic zinc must have been produced. These experiments certainly need further elucidation.

Zinc sulphide heated with carbon and lime produces metallic zinc, calcium sulphide being formed;<sup>1</sup> the decomposition is, however, incomplete, and is said by Berthier to depend on the temperature.

Iron decomposes zinc sulphide at a bright red heat, with the formation of ferrous sulphide and zinc vapour; it is probable that a small amount of zinc sulphide will, however, unite with the iron sulphide, and thus escape decomposition.

According to Percy,<sup>2</sup> tin only decomposes zinc sulphide imperfectly at bright redness.

Antimony appears not to decompose zinc sulphide, according to Percy's experiments,<sup>3</sup> and lead only very imperfectly.<sup>4</sup> Copper decomposes it, according to the same authority,<sup>5</sup> at a white heat with the formation of a copper regulus.

Hydrogen has no effect upon zinc sulphide, according to Berthier.<sup>6</sup> According to Morse,<sup>7</sup> zinc sulphide can be apparently sublimed in a current of hydrogen. This circumstance is said to be caused by the reduction of the sulphide in the presence of excess of hydrogen with the formation of sulphuretted hydrogen, whilst at a lower temperature the volatilised metal takes the sulphur up again from the latter gas.

According to Berthier, zinc oxide and zinc sulphide, when heated together in any proportions, form fusible oxysulphides.

Percy<sup>8</sup> deduces, from some rather imperfect experiments, that sulphide and oxide of zinc mutually decompose each other at high temperatures, like sulphide and oxide of copper. With suitable proportions it would accordingly be possible to reduce the whole of the zinc with the formation of sulphur dioxide, whilst any excess of sulphide or oxide would remain in the residue. If Percy's deductions are correct, considerable quantities of zinc might thus be won; but his experiments require confirmation.

Zinc sulphide and cuprous oxide appear, from similarly incomplete experiments of Percy's,<sup>9</sup> to decompose each other, a button looking like copper, and a regulus being produced.

Zinc sulphide and litharge, heated together in suitable proportions, decompose each other, according to Berthier,<sup>10</sup> the products being lead, zinc oxide and sulphur dioxide. If the zinc oxide thus

<sup>1</sup> Berthier, *Tr. d. Essais*, vol. ii. p. 570.

<sup>2</sup> *Op. cit.* p. 543.

<sup>4</sup> *Op. cit.* p. 543.

<sup>6</sup> *Annales des Mines* (3), vol. xi. p. 46.

<sup>8</sup> *Op. cit.* p. 542.

<sup>9</sup> *Op. cit.* p. 544.

<sup>3</sup> *Op. cit.* p. 543.

<sup>5</sup> *Op. cit.* p. 544.

<sup>7</sup> *Chem. Ztg.* 1889, p. 179.

<sup>10</sup> *Op. cit.* vol. i. p. 403.



formed is to form a liquid mass with the excess of lead oxide, there must be 25 times as much lead as zinc oxide present; in these proportions a resin-like glassy slag is obtained. By heating a mixture of 24.08 grams of blende with 55.78 grams of litharge, Berthier obtained 29.2 grams of blackish-grey hard lead, with 1.8 per cent. of sulphur and 0.8 per cent. of zinc. Above the lead was a layer consisting of sulphides and oxides of lead and zinc together with sulphur.

Carbon dioxide has no action upon zinc sulphide, even at a red heat.

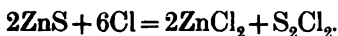
When zinc sulphide and nitre are heated together, zinc oxide and potassium sulphate are produced.

By fusing alkaline carbonates with zinc sulphide at a red heat, mixtures of zinc oxide, zinc sulphate and alkaline sulphides are obtained.

Zinc sulphide and lime only decompose each other, according to Berthier,<sup>1</sup> in the presence of carbon. By heating 6.32 grams calcium carbonate and 6.03 grams zinc sulphide to a very high temperature, five-sixths of the zinc was volatilised, whilst the residue, weighing 4.6 grams, contained but little sulphide of zinc. Percy<sup>2</sup> heated up to a white heat 35 grams of blende with 35 grams of lime, without carbon, in a lime crucible placed inside a graphite pot and separated from it by a layer of lime, and obtained a pale brown, porous, imperfectly fused mass, weighing 27 grams; the latter yielded a little sulphide (calcium polysulphide) to boiling water, and dissolved in hydrochloric acid with the evolution of sulphuretted hydrogen, the resulting solution containing zinc. The above experiment does not, however, prove whether the decomposition of sulphide and oxide of zinc is in any degree a complete one. According to Prost,<sup>3</sup> equivalent quantities of lime and zinc sulphide react at 1200°, but 75 per cent. excess of lime brings about complete decomposition of the sulphide at 1250° C.

Zinc sulphide is insoluble in water, but soluble in weak mineral acids (best in nitric acid). Hot and strong sulphuric acid decomposes it with separation of sulphur and liberation of sulphur dioxide.

In the cold chlorine and chlorine water have but little action on zinc sulphide. Chlorine gas, however, attacks it readily at 30° to 40° C. or at higher temperatures, forming thereby zinc chloride and sulphur chloride, thus:—

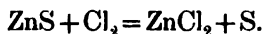


<sup>1</sup> *Op. cit.* vol. ii. p. 570.

<sup>2</sup> *Op. cit.* p. 546.

<sup>3</sup> *Bull. de l'Assoc. Belge des Chimistes*, X. 6, pp. 246–263.

Dorsemagen states that the action begins at 30°–40° C. with liberation of sulphur; but according to Ashcroft<sup>1</sup> the reaction only commences at temperatures above 600°, sulphur being liberated according to the equation:—



Zinc sulphide is decomposed by an aqueous solution of lead chloride, the products being zinc chloride and lead sulphide. The reverse action takes place on fusing the two latter in the dry state.

### ZINC SILICATE ( $\text{Zn}_2\text{SiO}_4$ )

This compound occurs anhydrous in nature as willemite ( $\text{Zn}_2\text{SiO}_4$ ), and hydrated as hemimorphite ( $\text{Zn}_2\text{SiO}_4 + \text{H}_2\text{O}$ ). As already stated, it is obtained artificially by heating zinc oxide and silica to a white heat. The bisilicate can be got in the same way. All these silicates are hard to melt, the bisilicate remaining solid in Percy's experiments even at the most intense white heat.

By heating to whiteness with carbon, both the natural and the artificial silicate can be completely reduced to metallic zinc. According to experiments of Percy,<sup>2</sup> complete reduction is also obtained when the finely powdered silicate is heated without any admixture of carbon in carbon-lined crucibles, but the reduction is imperfect when the silicate is treated in fragments of the size of peas in such crucibles.

When zinc silicate is strongly heated with carbon and lime, the zinc is also completely reduced.

### ZINC CARBONATE ( $\text{ZnCO}_3$ )

This compound occurs in nature as smithsonite, and in the form of a basic hydrated salt as hydrozincite ( $3\text{ZnCO}_3 \cdot 2\text{H}_2\text{O}$ ). It is produced artificially as a basic hydrate by driving off the ammonia from a solution of zinc oxide in ammonium carbonate. A number of carbonates and hydrated carbonates are also known. Neutral zinc carbonate is obtained by reaction between soluble zinc salts and alkaline carbonates under pressure, or by action on zinc sulphate with excess of potassium bicarbonate (Roscoe and Schorlemmer's method). The hydrated carbonate  $2\text{ZnCO}_3 \cdot \text{H}_2\text{O}$  can be got by digesting basic zinc carbonate with ammonium bicarbonate. The neutral carbonate is soluble to the extent of 1 in 189 parts by weight of carbonic acid under a pressure of 5 atmospheres.

<sup>1</sup> *On Sulphide Ore Treatment*.

<sup>2</sup> *Op. cit.* p. 537.

The several hydrated basic carbonates are obtained by addition in varying amounts of carbonates, bicarbonates and sesquicarbonates of potassium and sodium to solutions of neutral zinc salts, or by loss of ammonia from solutions of zinc hydroxide in ammonium carbonate.

All the carbonates lose carbon dioxide when heated.

### ZINC SULPHATE ( $\text{ZnSO}_4$ )

This salt crystallises as  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , in which hydrated condition it occurs naturally as goslarite. It is prepared artificially by dissolving zinc, zinc oxide or zinc carbonate in sulphuric acid, as also by roasting zinc sulphide with access of air at the lowest possible temperature.

Commercial zinc vitriol has the same composition as goslarite, and is got by crystallisation of its solution below  $30^\circ \text{C}$ . It is readily soluble in water, loses 6 molecules of water at  $100^\circ \text{C}$ ., and the last molecule at  $200^\circ \text{C}$ .

The three sulphates,  $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$ , and  $\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$ , are obtained by crystallising solutions of zinc sulphate at  $30^\circ$ ,  $40-50^\circ$ , and  $0^\circ \text{C}$ . respectively, the last in acid solution.  $\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$  is thrown out as a crystalline powder by addition of strong sulphuric acid to boiling zinc sulphate solution, and  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$  is left after heating the hepta-hydrate to  $100^\circ \text{C}$ .

Anhydrous zinc sulphate,  $\text{ZnSO}_4$ , is a white brittle body which is formed by roasting zinc blende at low temperatures. It unites with water to form the hepta-hydrate, and on heating loses sulphur dioxide and oxygen (in part sulphur trioxide) to form first a basic sulphate and finally zinc oxide. Ingalls<sup>1</sup> found 2.68 per cent. of sulphur in the residue after heating 10 grams of neutral zinc sulphate at  $900^\circ \text{C}$ . for 1 hour, but this sulphur was completely driven off after heating for another hour at this temperature. Heated at  $700^\circ \text{C}$ . for 2 hours 10 grams of sulphate left a residue containing 14.78 per cent. of sulphur.

Several basic sulphates are known, *e.g.*  $\text{ZnSO}_4 \cdot \text{ZnO}$ ;  $\text{ZnSO}_4 \cdot 3\text{ZnO}$ ;  $\text{ZnSO}_4 \cdot 4\text{ZnO}$ . These are formed in part by the decomposition of the sulphate produced by roasting zinc blende. The existence of an acid sulphate  $\text{ZnSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  has been proved by Kobell.<sup>2</sup>

Carbon decomposes zinc sulphate on heating; at a red heat a mixture of carbon and zinc oxide is left behind, sulphur dioxide and

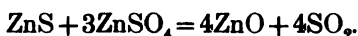
<sup>1</sup> *Production and Properties of Zinc*, New York and London, 1902, p. 155.

<sup>2</sup> *Journ. pr. Chem.* xxviii. p. 492.

carbon dioxide being evolved; at a higher temperature the carbon reduces the zinc oxide to metal. If on the other hand a mixture of zinc sulphate and carbon is heated sharply to whiteness, zinc sulphide and carbon monoxide are formed.

Ingalls<sup>1</sup> heated a mixture of 10 grams of zinc sulphate with 1 gram of wood charcoal for 2 hours at a dull red heat, and found that the residue contained 9·58 per cent. of sulphur.

When sulphide and sulphate of zinc are heated in equivalent quantities, zinc oxide and sulphur dioxide are formed, thus:—



Ingalls<sup>2</sup> heated 4 grams of zinc sulphide with the equivalent quantity of sulphate for 1 hour 10 mins. at a red heat, gradually rising to a white heat, and found 0·76 per cent. of sulphur in the residue.

Zinc is not precipitated from solutions by heavy metals.

A solution of zinc sulphate is decomposed by an electric current, zinc going to the cathode, and the acid radical to the anode.

### ZINC SULPHITE ( $\text{ZnSO}_3$ )

Neutral zinc sulphite is produced by the action of a solution of sulphur dioxide in water (sulphurous acid,  $\text{H}_2\text{SO}_3$ ) on zinc or its oxide. Moist zinc oxide and sulphur dioxide give the sulphite  $\text{ZnSO}_3 \cdot 2\text{H}_2\text{O}$ . This salt is almost insoluble in water; it is decomposed at 200° C. into zinc oxide, sulphur dioxide and water, and is oxidised fairly quickly in air to the sulphate. It dissolves in excess of sulphurous acid, forming a bisulphite of zinc, the solution of which loses sulphur dioxide on heating and deposits the neutral sulphite.

### ZINC CHLORIDE ( $\text{ZnCl}_2$ )

This salt is produced by heating zinc oxide to redness in chlorine, by burning zinc in chlorine, or by acting on the moistened metal with chlorine, by heating a mixture of anhydrous zinc sulphate with chloride of sodium or calcium, by dissolving zinc, zinc oxide or zinc carbonate in hydrochloric acid, evaporating the solution to dryness and subliming the hydrate,  $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ ; or by replacing the electro-negative metals from their molten chlorides. Solutions of sodium chloride and zinc sulphate give by double decomposition zinc chloride

<sup>1</sup> *Op. cit.* p. 155.

<sup>2</sup> *Op. cit.* p. 155.

and sodium sulphate, and the latter can be crystallised out by cooling. Ferric chloride acts on zinc oxide, forming zinc chloride and ferric hydroxide.

Zinc chloride melts to a brown liquid at  $262^{\circ}$ , and boils at  $718^{\circ}$ — $719^{\circ}$  C. It volatilises without decomposition at a red heat. It is easily soluble in water, and the metal cannot be thrown out from solutions by heavy metals.

Zinc chloride is very hygroscopic and retains water strongly. The hydrate,  $\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ , is obtained from watery solution. From this hydrate it is very hard to get the salt with less than 3 to 5 per cent. of water, since hydrogen chloride is given off and a basic salt is formed. Heating in vacuo is said to withdraw all the water without any decomposition taking place.

Basic zinc chloride, or zinc oxychloride, is obtained by dissolving zinc or zinc oxide in strong solutions of zinc chloride, and by evaporation of aqueous solutions of zinc chloride to a certain point. It is also formed, besides zinc hydroxide, by precipitation of zinc chloride solutions with milk of lime or magnesia, and to some extent by the chloridising roasting of zinc ores. The oxychlorides of zinc are volatile at a high temperature, though it is quite possible that they are partly decomposed into zinc oxide and chlorine. Of the many basic chlorides, those which have been closely investigated are  $\text{ZnCl}_2 \cdot 3\text{ZnO}$ ;  $\text{ZnCl}_2 \cdot 6\text{ZnO}$ ; and  $\text{ZnCl}_2 \cdot 9\text{ZnO}$ .

When zinc chloride is free from water, from lead and other chlorides, it can be melted in iron pots.

### ALLOYS OF ZINC

Zinc alloys with many metals, for example, gold, silver, copper, lead, nickel, tin, antimony.

It has greater affinity for silver and gold than lead has; silver can therefore be extracted from molten argentiferous lead by the aid of zinc. A mixture of various alloys of lead, zinc and silver is thus produced, out of which the greater part of the lead may be liquated. If both the lead and the zinc are free from copper, or if a small proportion of aluminium is added to the zinc, a fairly rich zinc-silver alloy can be obtained. From the triple lead-silver-zinc alloy the zinc may be removed by distillation, by oxidation, by slagging, and by treatment with dilute sulphuric acid; the latter method can also be used for the zinc-silver alloys, as may also distillation and electrolysis.

Zinc is therefore used for enriching poor argentiferous lead and for collecting the silver in alloys of either lead zinc and silver or of zinc and silver.

By heating zinc alloys to the boiling point of zinc, the latter may be vaporised and obtained by condensing the vapours.

If water vapour is passed into a red-hot, molten lead-silver-zinc or lead-zinc alloy, it is decomposed by the zinc present, hydrogen being evolved and zinc oxide formed, whilst silver-lead or lead, as the case may be, remains behind.

By fusing the above zinc alloys with lead oxide, the zinc may be separated out as oxide.

By fusing lead-zinc alloys or lead-silver-zinc alloys with common salt, the zinc is converted into chloride, the other metals remaining unchanged.

By the aid of a suitable electrolyte, with a proper strength of current, zinc may be electrolytically dissolved from its alloys and thrown down at the cathode.

### ZINC ORES

The most important ores of zinc are zinc blende, calamine and hemimorphite. The other ores, hydrozincite, zincite and franklinite, are of far less metallurgical importance, on account of their scarcity.

### ZINC BLENDE OR SPHALERITE ( $\text{ZnS}$ )

Zinc blende forms at present the main source of zinc production. It rarely consists of pure sulphide of zinc, but generally contains manganese and iron, together with smaller quantities of the sulphides of cadmium and silver. Less frequently it contains mercury, gold, lead and tin. Pure zinc blende contains 67.15 per cent. of zinc. The ratio of iron present varies generally from 1 per cent. to 18 per cent.; that of cadmium may go up to 5 per cent.

The varieties of zinc blende are common blende or "black jack," which contains little or no iron; Marmatite, with 10 per cent. or more of iron present as sulphide; Wurtzite ( $6\text{ZnS}, \text{FeS}$ ), which occurs at Oruro in Bolivia and at Przibram in Bohemia; and Przibramite, which contains up to 5 per cent. of cadmium.

Zinc blende is found in most countries. In Europe the chief localities are Germany (the Harz, the Erzgebirge, Silesia, Westphalia), the Rhine district (Hessen-Nassau and Baden), Austro-Hungary (Carinthia, Hungary, Tyrol, and Bohemia), Italy (Sardinia, Lombardy).

and Piedmont), Belgium (Corphalie, Bleyberg, Welkenraedt, and Engis), England (Wales, Cornwall, Cumberland, Isle of Man, Anglesea, Denbighshire, and Shropshire), France (Brittany, Gascony, Languedoc, and Provence), Spain (Santander, Murcia), Sweden (Ammeberg and Copparberg), Russia (Allagir, Kutais, and Petrowsk), Greece. In Africa, Algeria; in Australia, New South Wales (Broken Hill) and Tasmania; in Asia, Siberia (Altai); in America, the United States (Arkansas, Utah, New Mexico, Tennessee, Virginia, Kentucky, Iowa, New Jersey, Missouri, Pennsylvania, Wisconsin, and Colorado), in Canada, Mexico, and South America (Huanchaca).

Blende is frequently accompanied by pyrites, chalcocite, galena, and various arsenides and antimonides, as also by quartz, calcite, dolomite, siderite, and in many instances by mica, chlorite and hornblende.

#### CALAMINE, SMITHSONITE, OR ZINC SPAR ( $\text{ZnCO}_3$ )

This ore was formerly the chief source of zinc. At present a great number of the true deposits of calamine are exhausted, whilst others that carried calamine in the shallower portions have passed into blende in depth. The quantity of this ore that is treated has hence fallen off considerably.

Calamine is rarely pure carbonate of zinc, but contains as a rule the isomorphous carbonates of cadmium, iron, and manganese. If quite pure, it would contain 52 per cent. of zinc, whilst the impure ore containing other carbonates may have under 40 per cent. of zinc; the proportion of cadmium may go up to several per cents.

Calamine occurs in Europe, in Germany (Upper Silesia, Rhine districts, Westphalia, and Baden), Austro-Hungary (Carinthia), Belgium (Moresnet, Bleyberg, Welkenraedt, Corphalie, and Philippeville), France (Brittany, Gascony, and Languedoc), Russia (Poland), Greece (Laurium), Italy (Sardinia and Piedmont), Spain (Santander, Murcia, Cordoba, Granada, Carthagena, Almeria, and Castillon); in Turkey (Brussa, Smyrna); in America, in the United States (Missouri, Virginia, New Jersey, Tennessee, Arkansas, Pennsylvania, Wisconsin, and New Mexico); in Africa, in Algeria and Tunis.

This ore is generally intermixed with clay, brown iron ore, red hæmatite, galena, dolomite, and calcite; what is known as white calamine contains clay as its chief impurity, whilst red calamine contains anhydrous and hydrated oxides of iron and oxide of manganese.

**ELECTRIC CALAMINE, HEMIMORPHITE, OR ZINC SILICATE**  
( $\text{Zn}_2\text{SiO}_4 + \text{H}_2\text{O}$ )

This ore contains 53·7 per cent. of zinc when pure, and is often intermixed with the last-named. It occurs in considerable quantities in Altenberg, near Aix-la-Chapelle, in Sardinia (Iglesias), Spain, Tunis (Zaghouan), and the United States of North America (New Jersey, Pennsylvania, Missouri, Kansas, Virginia, and Wisconsin).

**WILLEMITE, TROOSTITE OR HERBETINE ( $\text{Zn}_2\text{SiO}_4$ )**

This ore is an anhydrous silicate, and occurs with calamine in important quantities at Altenberg and in the United States (Stirling Hill, Franklin Furnace, and New Jersey). It contains 58 per cent. of zinc.

**HYDROZINCITE OR ZINC BLOOM ( $\text{ZnCO}_3 + 2\text{ZnH}_2\text{O}_2$ )**

This ore occurs in small quantity in many deposits of zinc ore : it is abundant near Santander and Guipuzcoa in Spain, and less so at Bleiberg and Raibl in Carinthia. It contains 57·1 per cent. of zinc.

**ZINCITE OR RED ZINC ORE ( $\text{ZnO}$ )**

This ore is coloured red by oxide of iron, and always contains oxide of manganese, the proportion of manganese going up to 12 per cent. It occurs abundantly, mixed with Willemite and Franklinite at Stirling Hill and Franklin Furnace in the State of New Jersey. When pure it contains 80·2 per cent. of zinc.

**FRANKLINITE ( $\text{Fe,Zn,Mn})\text{O}, (\text{Fe Mn})_2\text{O}_3$**

This ore occurs in large quantities at Stirling Hill and Franklin Furnace in New Jersey ; it contains 11 to 21 per cent. of zinc.

Though metallurgically unimportant, mention may be made of Voltzite ( $\text{ZnO}, 4\text{ZnS}$ ), found at Pontgibaud in France and at Joachimsthal in Bohemia, of Goslarite ( $\text{ZnSO}_4, 7\text{H}_2\text{O}$ ), a mineral formed in old mines by the decomposition of zinc blende, and of Ferrogoslarite, a sulphate of zinc and iron which occurs in Missouri and Kansas.

**METALLURGICAL PRODUCTS CONTAINING ZINC**

Besides its ores, certain furnace products form sources of zinc extraction. Among these are the so-called *furnace calamine*



(furnace deposits obtained during the smelting of lead, copper, silver and iron ores containing zinc, and which are largely composed of zinc oxide), zinciferous flue dust, zinc fume, zinc dross, roasted silver ores containing zinc. Zinc is obtained as a bye-product in the treatment of alloys of zinc and silver, zinc, silver and lead, and zinc, silver, copper and lead.

### THE EXTRACTION OF ZINC

Zinc may be extracted from ores and furnace products by :—

1. The Dry way.
2. The Wet way, up to a certain point (combined wet and dry way).
3. Electro-metallurgical methods.

Metallic zinc can only be obtained in the dry way and electro-metallurgically. As zinc cannot be separated from its solutions by means of any of the metals that are unoxidised at the ordinary temperature, the wet method only admits of the production of compounds of zinc (zinc oxide), from which the metal must be extracted in the dry way. Wet methods can therefore only be considered as accessory processes in the dry method of zinc extraction.

The extraction of zinc from ores and furnace products in the dry way is performed by converting the zinc into oxide (unless it already exists as oxide or silicate in the ores, or as an alloy in furnace products), followed by the reduction of the oxide or silicate by means of carbon. Furnace products which consist of mixtures of zinc oxide and metal are submitted to direct reduction. From alloys with metals less volatile than zinc, the latter is obtained by simple distillation. The direct extraction of zinc from its sulphide by heating the latter with carbon and lime has not proved successful.

The extraction of zinc by the combined wet and dry methods is performed by dissolving out the zinc, converting the zinc in solution into oxide, and then reducing the latter by means of carbon. The electrolytic extraction of zinc is performed by obtaining the zinc in the form of aqueous solutions, from which zinc is separated by means of the electric current. If zinc exists in the form of alloys the latter may be used as anodes in the electric circuit. Of all the above methods, the dry way should be given the preference whenever the ores or furnace products are sufficiently rich in zinc. In spite of the great deficiencies, to be considered below, of the latter process, no success has attended attempts to replace it advantageously by combined wet and dry, or electro-metallurgical methods. The combined

wet and dry method has been tried experimentally on poor ores, but has hitherto failed on account of a number of defects and of the high expense attached to it. It has only been employed definitely in cases in which the object was not the extraction of metallic zinc, but the separation of zinc from other metals or metallic compounds, so that the zinc is obtained as a bye-product in the form of commercial compounds, such as sulphate, chloride, basic carbonate, or oxide of zinc. It is not, however, quite impossible but that it may find employment in zinc extraction proper as an auxiliary to the dry method for the preparation of compounds rich in zinc from ores or products poor in that metal. The electro-metallurgical method has, up to the present, only been used on an experimental scale, and with varying results upon zinc ores proper, containing no other valuable metal except zinc. Although the technical possibility of this process has been proved for such ores by continuous operation for a certain time, it is still to-day an open question whether it is superior to the dry method. It can be used with advantage for alloys which form soluble anodes in the electric circuit. It has also been used for the extraction of the zinc from pyritic residues, and from intimate mixtures of argentiferous zinc and lead ores which cannot be completely separated by dressing.

### *Purification of Zinc*

The zinc that has been obtained by the dry or combined wet and dry methods is in most cases contaminated by impurities, such as lead and iron, which interfere with the technical applications of the former metal. It therefore needs before use a purification, known as refining. This refining is executed in the dry way.

## EXTRACTION OF ZINC IN THE DRY WAY

### *The Extraction of Zinc from Ores*

The method of extracting zinc in the dry way, which has been used up to the present for ores, depends upon the property of carbon and bodies containing carbon to separate metallic zinc from the oxides and silicates of that metal at a high temperature. The recent suggestions to decompose sulphide of zinc by means of iron have not yet been put into execution.

The ores from which zinc is extracted are the oxide, silicate, carbonate and sulphide. The ores consisting of oxide and silicate contain zinc in a combination suitable for reduction. Ores containing the carbonate can be converted into oxide by simple calcination.

those that contain the sulphide by means of an oxidising roasting. The complete reduction of oxide of zinc only takes place at very high temperatures. It begins even below the boiling point of zinc at a moderate red heat, but is only complete at a bright redness approaching a white heat. It is therefore necessary to increase the temperature to the boiling point of zinc, so that the zinc is separated in the gaseous condition, and requires to be condensed to liquid zinc.

The chemical reactions in extracting zinc from its oxide and silicate consist in the formation of zinc and carbon monoxide, when the former compounds are heated to the necessary temperature with carbon. Carbon monoxide, however, also has a reducing action upon the oxide of zinc, carbon dioxide being produced. Carbon dioxide, which oxidises zinc at a red heat, is again reduced immediately upon its formation to carbon monoxide by means of the carbon, which must be present in excess, the carbon monoxide thus formed again reducing a further amount of zinc oxide. Oxidation of the zinc by carbon dioxide is therefore impossible in the presence of a sufficient excess of carbon. It is unknown to what extent carbon monoxide assists in the reduction of zinc oxide. The more intimate the mixture of zinc oxide with carbon, the better does the reduction of the former take place.

The gaseous zinc must be condensed to the liquid state; as zinc vapours are oxidised by air, water vapour and carbon dioxide, they must not be allowed to come into contact with these gases. The condensation of zinc vapour to liquid zinc, which forms the most difficult portion of the process of zinc extraction, takes place between definite limits of temperature, and is then only possible when the zinc vapour is not too greatly diluted by other gases. If the temperature falls below the melting-point of zinc ( $415^{\circ}$  C.), the zinc vapours condense to a powder known as *zinc fume*. If the temperature greatly exceeds  $550^{\circ}$  C., the zinc remains in the gaseous form. If the zinc vapours are mixed with foreign gases, their condensation to liquid zinc is thereby rendered more difficult. When a certain point of dilution with foreign gases is reached, the zinc vapours will no longer condense to liquid zinc, but form zinc fume on cooling down. The temperature at which zinc vapours, produced in practice by the reduction of zinc oxide by carbon, and therefore diluted with carbon monoxide, will condense to liquid zinc, lies between  $415^{\circ}$  and  $550^{\circ}$  C. The necessity of employing a temperature exceeding the boiling point of zinc in the extraction of that metal, the readiness with which zinc vapours are oxidised by air, carbon dioxide and water vapour, and especially the difficulty of condensing into a

liquid form the vapours of zinc diluted by other gases, cause the extraction of zinc to be one of the most difficult and most imperfect of all metallurgical operations. The readiness with which zinc vapour is oxidised compels the process of reduction to be carried on with the exclusion of air. The high temperature required for the reduction renders necessary the employment of a first-class fire-resisting material for the construction of the apparatus of reduction. The latter are at present closed vessels, such as tubes or muffles, made of fireclay, with a comparatively small capacity, and destroyed with comparative ease, so that the operation is attended with high costs in fuel and labour. As it is not possible to completely condense zinc vapours, as the walls of the apparatus used in reduction are to a certain extent permeable by gases and readily fractured, as the material of the retorts always retains a certain quantity of zinc in the form of an aluminate, and as a certain quantity of metal always remains in the residues, the extraction of zinc is accompanied with considerable losses of metal—amounting in favourable cases to about 10 per cent. of the zinc contents of the ore, and in some cases rising to 25 to 30 per cent. For the above reasons, ores, the percentage of zinc in which falls below certain limits, cannot be treated with profit in the dry way.

It is therefore intelligible that attempts should have been made for a long time to improve this defective process of zinc extraction. The process of distillation can only be avoided by means of electrolysis or by reduction of the oxide or sulphide under such a pressure that the zinc separates out in the metallic state, because zinc is not precipitated in the metallic state from its solutions by any metal capable of existing at the ordinary temperatures, on account of its highly electro-positive character. Up to the present, however, the electrolytic extraction of zinc from its ores has not shown any superiority to the process of distillation as now carried on, nor have attempts to win the zinc in a liquid state under pressure led to the adoption of this process.

The numberless attempts to conduct the extraction of zinc oxide in reverberatory and blast furnaces have only given negative results as regards the production of zinc in the metallic state. By the employment of reverberatory furnaces zinc oxide only can be produced; by the employment of blast furnaces zinc vapour can certainly be produced; the latter has, however, even when heated air was employed, been found to be so greatly diluted by carbon monoxide and nitrogen, that it was impossible to condense it to the liquid state: only zinc fume could be separated from it. It appears,

therefore, that blast furnaces can only be used for the production from ores, of intermediate products rich in zinc, such as mixtures of zinc fume or zinc powder with small quantities of zinc oxide, from which latter the zinc can only be obtained by treatment in retorts. Hence it happens that improvements in the extraction of zinc in the ordinary way, apart from the calcination of zinc-blende, have been confined to the distillation process in closed vessels. Many such improvements may be mentioned, *e.g.*: the introduction of gas-firing and the use of natural gas (Kansas, Indiana), the improvement of the fireproof material of the vessels employed, the production of dense vessels by means of pressure, the increased size of the furnaces, the more perfect appliances for the condensation of zinc vapour and for the removal of the products of combustion from the interior of the zinc works.

In zinc extraction, as now practised, we have to distinguish:—

1. The preparation of ores for the process of reduction by calcining or roasting.
2. The reduction process proper, or the extraction of the zinc from the calcined ores.

#### 1. PREPARATION OF ORES FOR THE PROCESS OF REDUCTION

Zinc ores which contain the zinc in the form of oxide require no preparation. Silicates of zinc but rarely form an independent object of zinc extraction, as they generally occur together with calamine, and are therefore treated in the same way as that ore. If they occur by themselves, they have to be calcined for the removal of the water, which would otherwise exert an oxidising action upon the zinc during the process of reduction. No other preparation is required, because zinc is reduced from its silicates by means of carbon. Silicates free from water require calcination only to make them tender; ores of zinc that contain the metal as carbonate and sulphide—viz., calamine (including zinc bloom) and blende—must be converted into oxide before they can be reduced.

Zinc could be reduced from calamine without converting that ore previously into oxide; but in this case the process would not only be seriously delayed by the expulsion of the carbon dioxide and water from the ore and the loss of heat thereby occasioned, but the products, carbon dioxide and water vapour, would exert an oxidising influence upon the zinc vapour produced. To avoid these objections, it is absolutely necessary to drive off the water and the carbon dioxide from the calamine by a decomposing roasting known as burning or calcining.

This operation also possesses the great advantage of making the calamine more porous in structure. The reduction of zinc is hereby greatly facilitated, as an opportunity is afforded for the carbon monoxide to penetrate through all portions of the calamine thus rendered spongy, and to exert its reducing influence upon it.

As zinc blende cannot be directly reduced by carbon and lime, and as the proposed reduction with iron has not yet found application, it must be converted into zinc oxide by means of an oxidising roasting combined with a decomposing roasting that shall decompose the zinc sulphate formed.

### *Crushing Zinc Ores*

Of the above ores, zinc blende requires for its perfect calcination to be broken down to 0.04 to 0.08 inch mesh. Such crushing is also necessary in the case of pieces of blende which have been previously roasted in heaps, stalls or shaft furnaces before the final roasting. Whenever the blende is not produced in the form of concentrates by dressing works, the ores are crushed in rolls or edge mills after being previously broken with rock breakers in case of need. In Upper Silesia, Schwarzmänn's friction rolls have been found to be exceedingly effective and durable. As calamine can be burnt in lumps, it needs crushing only after burning. The Belgian method of zinc reduction requires more complete crushing than does the Silesian method. For hard ores, such as silicate of zinc and willemite, rolls, for soft ores, edge runners, ball mills and disintegrators are employed. When the ore has thus been obtained in the necessary form, it has to undergo a preliminary treatment, either by:—

- (a) Roasting or calcination of calamine.
- (b) Calcination of zinc blende.

### *(a) Roasting or Calcining of Calamine*

The object of this process is to remove carbon dioxide and water from the ore and to make it more porous. If other bodies containing water and carbon dioxide are mixed with the calamine, the water or carbon dioxide must be driven off from them also. This object is attained by heating the calamine to such a temperature that the carbonate of zinc shall be decomposed into zinc oxide and carbon dioxide, which temperature must also be sufficient to decompose any foreign carbonates present. Calamine gives up its carbon dioxide at a moderate red heat, whilst the complete decomposition of calcium carbonate requires bright redness. The loss of weight of pure zinc

carbonate on complete calcination amounts to 35·5 per cent. ; when all the water is removed from silicate of zinc, this loses 7·5 per cent. As a general rule, burnt calamine still retains more or less carbon dioxide, up to some 17 per cent.

As the zinc oxide produced by burning calamine gradually attracts carbon dioxide from the air, whilst lime does so rapidly, it is necessary to treat burnt calamine soon after it has been calcined, but immediately if it contains much lime. Calamine may be burned in heaps, stalls, shaft or reverberatory furnaces. As a rule, burning in heaps and stalls, for which lump ore is necessary, is to be avoided on account of the imperfect decomposition of the ore and the great waste of fuel. It is far more costly than the roasting of sulphides in heaps and stalls, as in the latter case the greater portion of the heat required for the operation is produced by the combustion of sulphur, whereas the heat required to remove water and carbon dioxide from calamine can only be produced by the combustion of extraneous fuel. Burning in heaps, with wood for fuel, is practised, according to Thum,<sup>1</sup> in the north of Spain ; burning in stalls, according to the same authority, in the mountains of the south of Spain, where wood is scarce. As a rule, lump calamine should be burnt in ordinary shaft furnaces or in shaft furnaces fired by means of external grates, crushed ores in reverberatory furnaces. The grate-fired shaft furnace has this advantage over the ordinary shaft furnace, that the ashes of the fuel do not intermix with the burnt ore, as is the case when fuel and ore come into direct contact inside the ordinary shaft furnace.

#### *Burning Calamine in Shaft Furnaces*

Calamine can be burnt in ordinary shaft furnaces with a comparatively small consumption of fuel, about 3·6 per cent. of the weight of the ore. This method admits of a high production, and requires but little labour ; it has, however, the objection that the burnt ore is mixed with the ashes of the fuel. If, moreover, the temperature rises too high, some zinc may be reduced. The fuels employed are lean coals low in ash, lignite low in ash, small coke low in ash, or small charcoal. These are charged in layers alternating with layers of calamine into the furnace. Together with the lump ore, the charge may contain a certain amount—15 or 20 per cent.—of ore fines.

The furnaces do not differ in any important respect from lime-kilns. The older furnaces have boshes and heavy retaining walls.

<sup>1</sup> *Bemerkungen über Zinkindustrie, Berg- und Hüttenm. Ztg.*, No. 17, p. 138, 1876.

The latter can be replaced with advantage by a casing of iron plates. The height varies, according to the nature of the ore, from 10 to 20 feet, and the diameter from 3 to 10 feet. The bottom is either flat, or provided with a cone. The output varies according to the nature of the calamine and its impurities, and the size of the furnaces. It is lower the greater the proportion is of lime and zinc-blende.

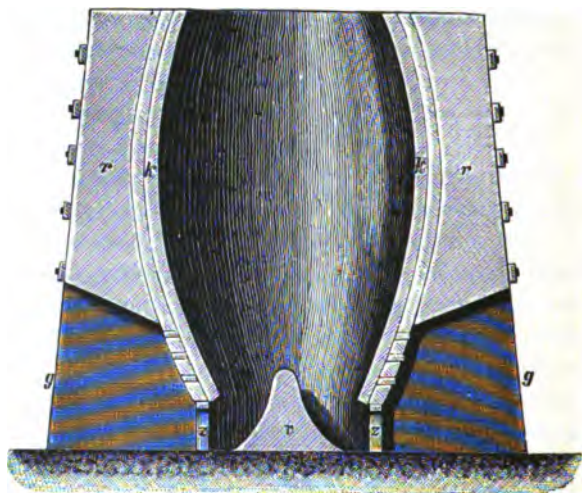


FIG. 1.

Under favourable circumstances, with large furnaces it may amount to 25 or 30 tons per 24 hours. The fuel consumption also varies with the impurities of the ore, and may lie between 3 and 6 per cent. of the weight of the raw ores. Calamine is burnt in shaft furnaces in Moresnet (Belgium), Dortmund, Laurion, Lehigh (Pennsylvania), and in the district of Iglesias (Sardinia). At Altenberg, near Moresnet, a mixture of calamine and silicate of zinc used to be burnt in a shaft furnace of the construction shown in Fig. 1,<sup>1</sup> in which *k* is the lining, *r* the retaining wall, *v* the cone, *g* arches, of which there are four, giving access to the draw-holes *z*. The shaft is 7 feet 3 inches in diameter at the throat, 9 feet 8 inches in the centre, and 5 feet 6 inches at the draw-holes. The cone is 3 feet 6 inches high; the height of the furnace from the point of the cone to the throat is 17 feet 6 inches. In this furnace calamine mixed with some silicate of zinc was burned with lean coals and coke smalls. The layers of ore, which alternated

<sup>1</sup> Thum, *Zinkhüttenbetrieb der Altenberger Gesellschaft, Berg- und Hüttenm. Ztg.*, p. 405, 1859, and p. 4, 1860; Kerl, *Metallhüttenkunde*, p. 433, 1881.



with layers of fuel, were 6 inches deep; 25 tons of ore were burned in 24 hours, during which time there were six drawings. The consumption of fuel was from 3 to 4 per cent. of the weight of the ore, and the loss of weight was about 27 per cent. of the weight of the raw ore. Any silicate of zinc, or any ferriferous calamine, were removed from the burnt ore by hand picking, and after crushing were burned again. At Montefiore, near Iglesias, where shaft furnaces are used which have a conical grate instead of a simple cone, small charcoal is used as fuel, from 4 to 6 per cent. of the weight of the ore being consumed.<sup>1</sup>

### *Burning Calamine in Grate-fired Shaft Furnaces*

Burning lump calamine in grate-fired shaft furnaces yields a product which is not contaminated by the ashes of the fuel, though it may at times contain small quantities of flue-dust. There is also less danger of the reduction and volatilisation of zinc, than when the ore comes in direct contact with the fuel; but, on the other hand, the fuel consumption is greater than in the simple shaft furnace. Only raw fuel or gas can be used for heating purposes. The consumption of raw fuel amounts, according to its nature and that of the ores, to some 6 to 9 per cent. of the latter. The furnaces are constructed like limekilns, fired by external grates; they are circular in horizontal section and contracted below. Their height is 8 to 16 feet; their diameter, in the upper widest

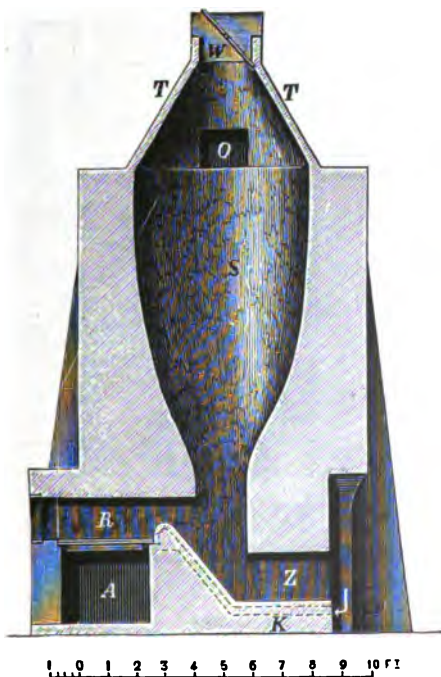


FIG. 2.

portion of the shaft, 5 feet to 5 feet 9 inches; at the narrowest portion, at the fireplace, 1 foot 8 inches to 2 feet. The number of fireplaces, which are disposed laterally about the lower portion of

<sup>1</sup> *Oesterr. Zeitschrift*, No. 40, 1886.

the furnace, is either 1 or 2. The output varies with the size of the furnace, the nature of the ores, and the number of fireplaces, lying between 6 and 14 tons per 24 hours. Such furnaces are employed in the south of Spain.

The construction of such a furnace, with but one fireplace, is shown in Fig. 2.<sup>1</sup> *S* is the shaft, *R* the firegrate, *Z* the opening

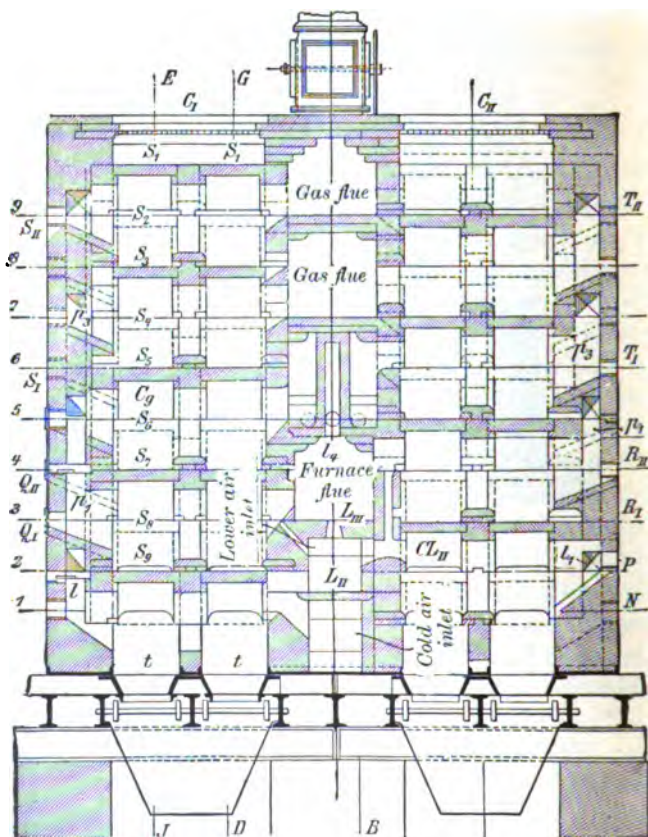


FIG. 3.

through which the burnt ore is drawn. The ashpit *A* below the fireplace is closed, air required for combustion entering through a flue *K* in the brickwork of the furnace, in which it is heated before it enters at the grate. The calamine to be burned is charged through the opening *O*. The throat of the furnace is covered by a conical hood *J*, which terminates in a short flue *W*, and is provided in its

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, p. 360, 1862.

upper part with a damper to regulate the draught. In such a furnace with one fireplace, 5 to 8 tons of burnt calamine are produced in 24 hours, with a coal consumption of 8 to 9 per cent. of the weight of the burnt ore. The raw ore loses at least 20 per cent. of its weight by burning. In a furnace of equal size, with two fireplaces, about 10 tons of burnt ore were obtained in 24 hours with the

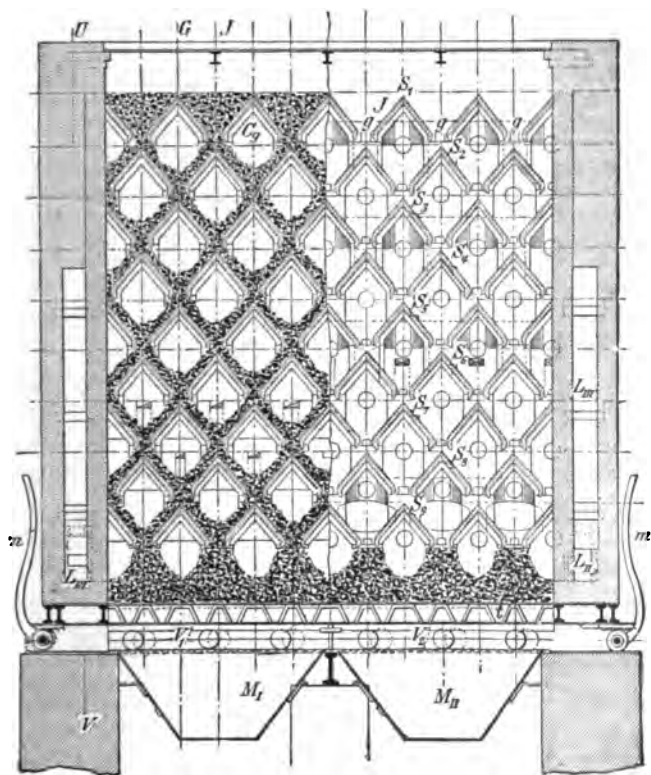


FIG. 4.

same fuel consumption. Six men are required per 24 hours to work the furnace.

At Ponte di Nossà in Italy, powdered calamine has been burnt recently in furnaces resembling those of Spirek which are used for the production of quicksilver from cinnabar (see Mercury). The arrangement of these is shown in Figs. 3 to 5.<sup>1</sup> The ore rests in the furnace on a number of sloping fire-clay tiles and fills up the space between these. At every withdrawal of ore from the bottom of the

<sup>1</sup> *The Mineral Industry*, 1902, p. 684.

furnace, the mass inside the furnace slips down a little. The lever  $m$  works a plate,  $V_1 V_2$ , in which are holes corresponding to those in the bottom of the furnace. When these holes are placed in correspondence, ore passes through them from the furnace to the boxes  $M_1 M_{11}$ . On the under side of the sloping tiles is a little upright fire-clay continuation, whereby a series of cells is formed, the intervals between them being filled with ore. The flame and gases from the fireplace (Fig. 5) traverse these cells lengthways, passing

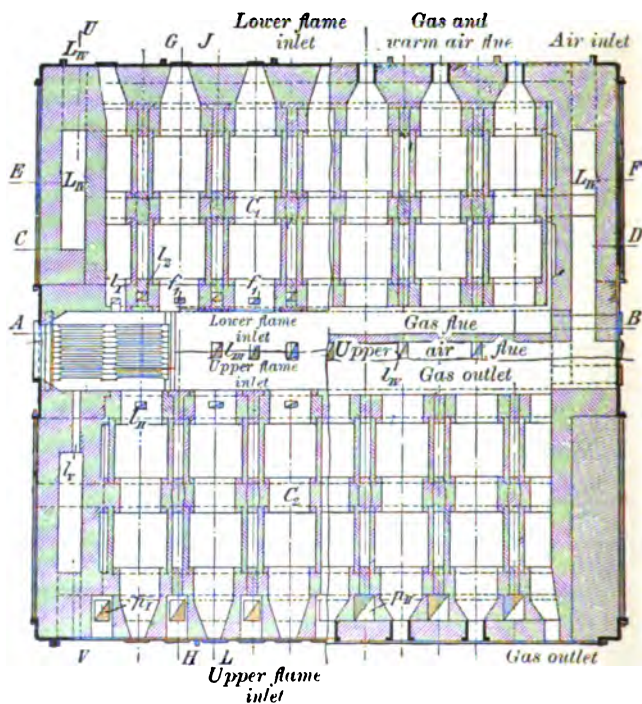


FIG. 5.

first through two channels (one over the other) along the middle wall of the furnace. This wall divides the furnace into two parts. After the flame has passed along the first row of cells next to the wall, it rises through a flue in the brickwork, passes through the next row of cells in the opposite direction, moves in the same manner to the next higher rows, and eventually escapes through flues in the middle wall. The air for combustion is warmed in special flues. By the circulatory arrangement just sketched, the tiles take up a large quantity of heat, and the ore resting on them is heated by direct

contact, by radiation from the tiles above, and by contact with the hot gases. If it is sought to reduce the oxide of iron in the calamine so as to fit the ore for magnetic treatment, then coal is mixed with the ore, and the upper gas flue and the lower air inlet are closed.

In a furnace of this description there were burnt at Ponte di Nossà, in 4 months, 1,145 tons of calamine, with a coal consumption of 8·5 per cent., 3 men and 2 boys being needed per furnace in an 8 hours' shift.<sup>1</sup> According to the latest information,<sup>2</sup> 1,525,800 tons of calamine, averaging 33·2 per cent. of zinc, were burnt in 5 months (Aug. 1, 1902, to Jan. 1, 1903). The burnt ore contained 42·9 per cent. of zinc, the coal consumption was 7·45 per cent. of raw ore, and the cost of calcining was 4·68 lire per ton. These results have occasioned the building of another furnace.

### *Burning Calamine in Reverberatory Furnaces*

In such furnaces ore fines alone can be burnt satisfactorily; lumps are far better burnt in either of the above shaft furnaces. Reverberatory furnaces require more fuel and labour than do shaft furnaces, but, if well constructed, yield as great an output as do grate-fired shaft furnaces, viz., 8 to 10 tons in 24 hours. Reverberatory furnaces are employed of various forms, viz., with fixed hearths, with movable hearths, furnaces independent of zinc reduction furnaces, and reverberatory furnaces which are heated by the waste heat of the zinc reduction furnaces. Those reverberatory furnaces which are worked independently are either gas-fired or fired by a grate. Wherever calamine is burnt at the mine, which is the better way whenever fuel is cheap there, and the ore has to be transported considerable distances to the smelting works, it is of course necessary to work the reverberatory furnaces independently. Wherever calamine is burnt at the smelting works, it is preferable to conduct the burning quite independently of the work of the reduction furnace, and to use the waste heat of the latter for warming the air used for combustion, or in the case of gas firing for heating up the gas. Only in those cases in which the furnace gases, after having thus been utilised, still retain sufficient heat to be able to expel water and carbon dioxide from the calamine, is it profitable to use them for burning this ore.

<sup>1</sup> *Resoconti della Associazione Mineraria Sarda*, vol. vi. 1901.

<sup>2</sup> *Rassegna Mineraria*, Torino, February 11, 1903.

*Independent Reverberatory Furnaces**Fixed Reverberatory Furnaces*

Such furnaces have to be worked as a general rule by hand-power. Only when labour is exceedingly dear is it possible to use with advantage fixed furnaces in which the ore is rabbled mechanically.

*Fixed Reverberatory Furnaces worked by Hand*

As a rule, the best furnace of this type for burning calamine is the long-bedded continuous-acting furnace, the so-called *Fortschauf-lungsofen*. In these the ore is charged at the coldest part of the furnace by the flue-bridge, and is shovelled gradually from this point to the hottest part of the furnace at definite intervals of time, until it is ultimately drawn out at the fire-bridge in the burnt state. Furnaces worked intermittently, in which the whole of the charge of ore which is to be burnt is charged in at one time, and is drawn out at one time when the operation is complete, are not to be recommended on account of their high cost for labour and fuel. Long-bedded calciners with only one hearth are to be preferred to furnaces of this type with two hearths lying one above the other, because working on the upper hearth is inconvenient, and when one of the hearths needs repairing the whole furnace must be let out. Furnaces with even two or three hearths, one above the other, should, therefore, only be employed when ground space is either very valuable or not to be got. The hearth either lies horizontally, or has a certain inclination (Ferraris furnace). The reverberatory furnace for burning calamine differs from those used for calcining the sulphides of iron, silver, copper or lead, in that it is shorter and narrower than the latter. It must not be forgotten that when the above-named sulphides are calcined, a considerable amount of heat is developed from the ores themselves; that the air required for their calcination enters by the working doors; and that as long as it is not in excess, it becomes itself a source of heat on account of its action upon the sulphides. On the other hand, when calamine is burnt, no heat is developed from the ores, nor is any excess of air necessary. In order to utilise the heat of the fuel to the best purpose, it is, therefore, necessary to have only as many working doors as are absolutely required for the satisfactory rabbling and turning over of the ores. It is also useless to give the hearth any excessive length or breadth, because the removal of the carbon dioxide requires a comparatively high tem-

perature, whilst no heat is developed from the ore, as occurs in the case of sulphides even close to the flue-bridge.

The length of the hearth should not exceed 40 to 43 feet. With a double hearth and a single fireplace, the length of the two hearths together should not exceed the above amount. When gas-firing is used, the length of the hearth may be somewhat longer, up to 46 feet for instance. The grate-fired furnace with double hearth at the works of the Altenberg Company is 40 feet, including the upper and lower hearths. Another direct-fired furnace at Letmathe, near Iserlohn, in Westphalia, in which calamine was formerly burnt, possessed two hearths lying one above the other, with a total length of 27 feet. The gas-fired furnaces of Ferraris, with inclined hearth, at Monteponi, near Iglesias, has a total length of 43 feet 6 inches. The breadth of the hearth should not exceed 8 feet, because otherwise the ore upon the hearth cannot be satisfactorily rabbled and turned over with working doors along one side only. For instance, the Letmathe hearth was 6 feet 2 inches wide, the hearth of the Altenberg Company's furnace was 7 feet 6 inches wide, whilst the gas furnace at Monteponi has a hearth 8 feet 2 inches wide. The height of the arch of the working chamber should be about 1 foot 4 inches to 2 feet at the outside. In order to utilise the heat to the utmost, it is advisable to incline the arch somewhat towards the flue-bridge, or else the hearth may have a gradual slope upwards, or may rise by steps towards the flue. The hearth may be made of ordinary brick, fire-brick being only required in the neighbourhood of the fire-bridge. The working doors are placed from 6 feet to 8 feet 2 inches apart, centre to centre. The quantity of calamine that can be burnt in 24 hours depends upon the nature of the impurities, the size of the furnace and the character of the fuel. It varies from 3 to 10 tons per furnace, the fuel consumption being between 10 and 15 per cent. of the weight of the raw ore. Each furnace requires two or three attendants per shift. The construction of a reverberatory furnace fired by grate, as built at the works of the Vieille Montagne Company, is shown in Figs. 6 and 7. The furnace has two hearths, *H* and *J*. The calamine is first dried on the arch *G* above the upper hearth, and is then let down on to that hearth by means of openings *o*, which can be closed when desired. After remaining 6 hours on that hearth, it is removed to the lower hearth through openings *p*, and after 6 hours further is emptied into the vaults *K* through the openings *q*. *F* is the fire-grate, *T* the flue through which the products of combustion pass into the stack, *a* are the working doors, which can be closed by sheet iron. Fig. 7 shows a plan of the upper hearth with



the openings *p*. The openings *q* for emptying the calamine into the cooling vaults lie at the opposite side of the lower hearth. In 24 hours 4 charges, weighing together 8 tons, are calcined in this furnace, with a consumption of 2.90 to 3.11 cubic feet of coal.<sup>1</sup>

At the works near Cilli, in Austria,<sup>2</sup> finely ground calamine is calcined in long-bedded furnaces, which are built in pairs with their

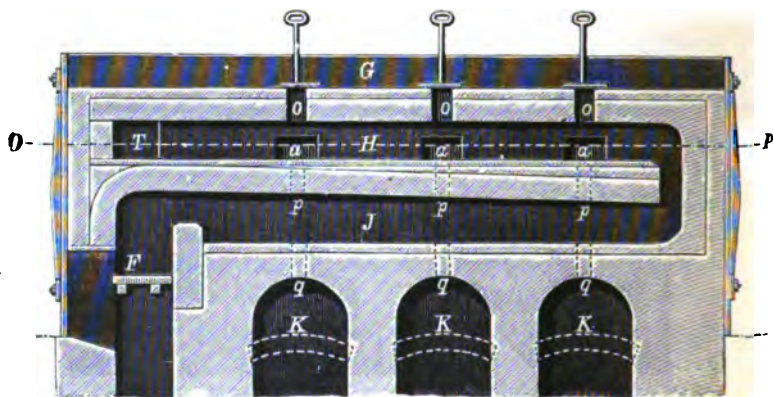


FIG. 6.

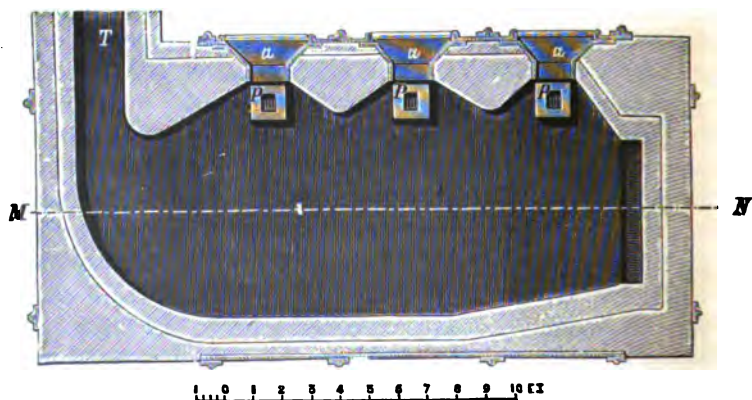


FIG. 7.

long sides adjoining, and with 4 working doors at the opposite sides. They are fired with lignite by means of special grates. In 24 hours 7 charges of 12 cwts. each are worked off.

At the Paul Works, near Rosdzin, in Upper Silesia, there are three long-bedded calcining hearths, one above the other, each of

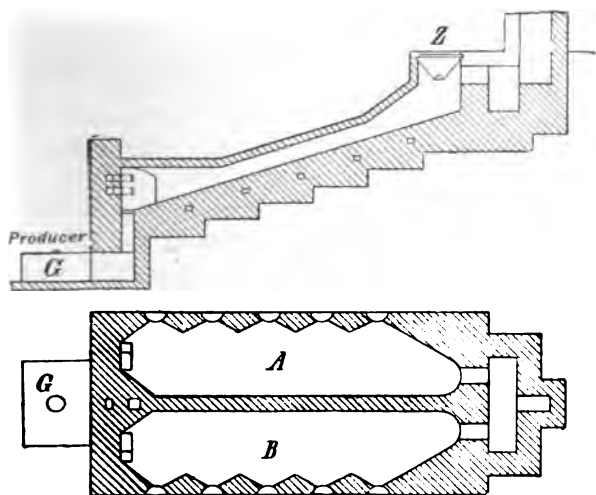
<sup>1</sup> Thum, *loc. cit.*

<sup>2</sup> *Berg- und Hüttenm. Ztg.* p. 31, 1894.



which has its own fireplace. Each hearth is 17 feet 10 inches long and 7 feet 10 inches wide. On each hearth 15 tons of calamine are calcined in 24 hours, with a consumption of 1.5 tons of coal. The furnace is worked by one man, taking a 12-hour shift. The arrangement of a reverberatory furnace fired by gas (the Ferraris furnace), as used at the Monteponi mines, is shown in Figs. 8 and 9.<sup>1</sup>

Two furnaces, A and B, with inclined hearths are built side by side with a back wall in common. There is a gas producer G on the Boëtius system, common to both furnaces. The ores are charged at the upper end of each furnace through a hopper Z and pass through the upper to the lower end. The double furnace treats 20 tons of ore in



FIGS. 8 and 9.

24 hours, with a consumption of Cardiff coals equal to 15.11 per cent. of the weight of the raw ore. Five men are employed to work the two furnaces. The ore loses 23 per cent. by calcination.

#### *Fixed Reverberatory Furnaces worked Mechanically.*

Such furnaces appear to be nowhere in use for calamine, unless the ore contains a considerable quantity of zinc blende mixed with it. Their use would only be indicated in the case of abnormally high wages. Under such circumstances the furnaces of O'Harra, Vol. I., p. 78, the Pearce furnace, Vol. I., p. 92, and the Brown Horseshoe

<sup>1</sup> Marx, *Zeitschr. für das Berg-, Hütten- und Salinenwesen*, vol. xl.

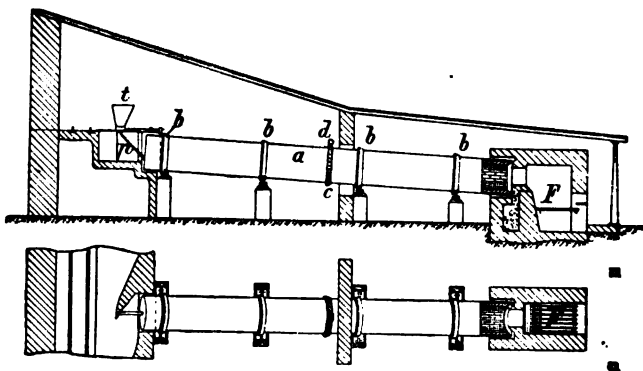
furnace, Vol. I., p. 98, would probably be the most suitable, because their output is far greater than that of fixed reverberatory furnaces worked by hand.

### *Reverberatory Furnaces with Movable Hearths.*

Calciners of this type, with fixed or movable rabbles, can scarcely be applied with advantage to the burning of calamine, on account of their comparatively small output. Many such furnaces may be mentioned, *e.g.*, that of Brunton,<sup>2</sup> which is used for the roasting of tin ores containing arsenical pyrites, and the furnace of Gibbs and Gelstharpe, Vol. I., p. 102, which is used for the chloridising roasting of cupriferos pyrites residues.

### *Reverberatory Furnaces with Movable Chambers.*

Such furnaces may be used when wages are high. They consist of rotating cylinders, which work either intermittently or con-



FIGS. 10 and 11.

tinuously. Furnaces worked intermittently, which are used with advantage for the calcination of copper ores, and of which the best known is the Brückner furnace, Vol. I., p. 103, have not been employed for the burning of calamine, as far as the author knows. Of the furnaces worked continuously, that of Oxland is used with advantage in the mining district of Iglesias. Figs. 10 and 11 show the construction of such a furnace as used at the Monteponi mine.<sup>3</sup>

In these figures *a* is the inclined rotating cylinder lined with fire-brick, *b, b* are friction rings resting on rollers, *c* is a spur wheel

<sup>1</sup> Imp. Ger. Pat. Class 40, No. 70807, 28 Dec. 1892.

<sup>2</sup> *Allgemeine Hüttenkunde*, p. 474.

<sup>3</sup> Marx, *loc. cit.*

worked by the tangent screw *d*, the latter being driven by a steam engine. The ore is charged through a hopper and falls from it on to a cast-iron plate, which forms the cover of the furnace, and upon which it is dried. Thence it passes through the hopper *t* into the tube *p*, through which it slips down into the cylinder. In consequence of the slow revolution of the cylinder, which turns 15 times in the hour, the ore gradually reaches the lower end, when it drops out in the calcined condition. *F* is the fire-grate. The mixing of the ore is promoted by four ploughs arranged inside the cylinder; 12 tons of ore are calcined in 24 hours, the consumption of Cardiff coal amounting to 12.41 per cent. of the weight of the raw ore. The loss of weight amounts to 28 per cent. Two men on a shift work these furnaces.

The arrangement at Monteponi is shown in Figs. 12 and 13.<sup>1</sup> The calamine is mixed in both the furnaces with 2 per cent. of coal in order to reduce the ferric oxide contained in it to the magnetic oxide. The burnt ore is screened, and the iron removed by magnetic treatment according to the method of Ferraris, the zinc content being brought up from 20.46 to 45 per cent. thereby. The length of the furnace is 42 feet 3 inches; the ore is fed in through a pipe 2 feet in diameter. The furnace is 3 feet 3 inches diameter in the inside, and is lined with wedge-shaped fire-proof bricks. It rests on 8 wheels, and is revolved 16 times an hour, the motion being caused by a worm wheel and tangent screw. The quantity of ore fed in is regulated by the position of the feed pipe, and the distance between the mouth of this pipe and the furnace. The ore passes through the furnace in 6 hours, and falls from the lower end, between the rim of the furnace and the grate, into a pit, where it is allowed to cool. The fire-grate, with blast beneath the grate, is shown at *C*; the horizontal section of the grate has an area of 10 square feet. The fuel is piled up on the grate so high that part of the combustible gases pass into the furnace, and are burnt there by the admission of air warmed by passing through the walls of the fireplace. The fire-bridge is tubular, and projects into the furnace, so that the rim of this is protected from the flames.

#### *Reverberatory Furnaces, heated by the Waste Heat of Zinc-Reduction Furnaces.*

Such reverberatory furnaces may be combined with Silesian or with Belgian zinc-reduction furnaces. With the former they are

<sup>1</sup> *Oester. Zeitschr. für Berg- u. Hüttenwesen*, 1892,

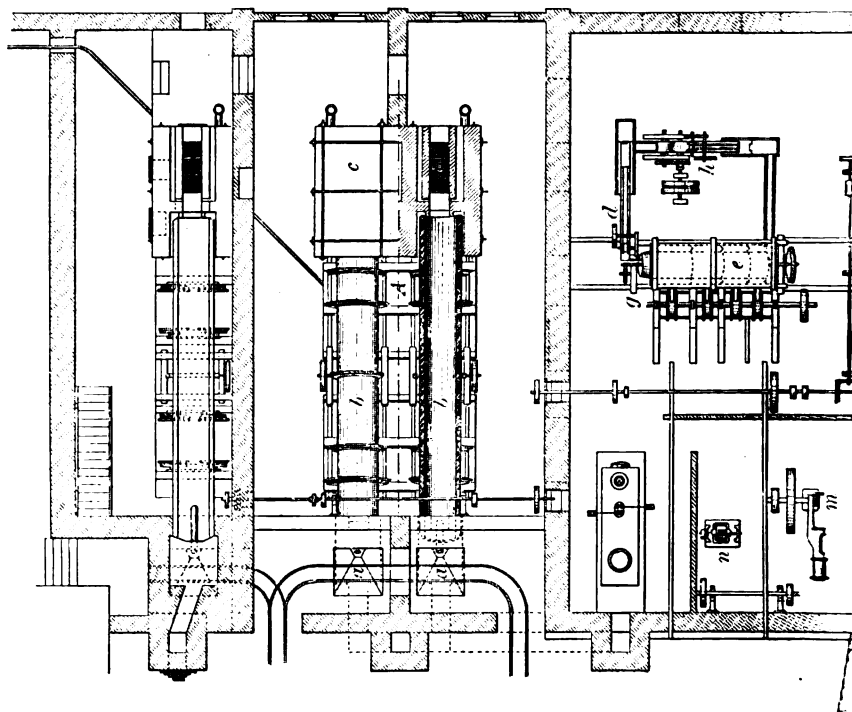


FIG. 12.

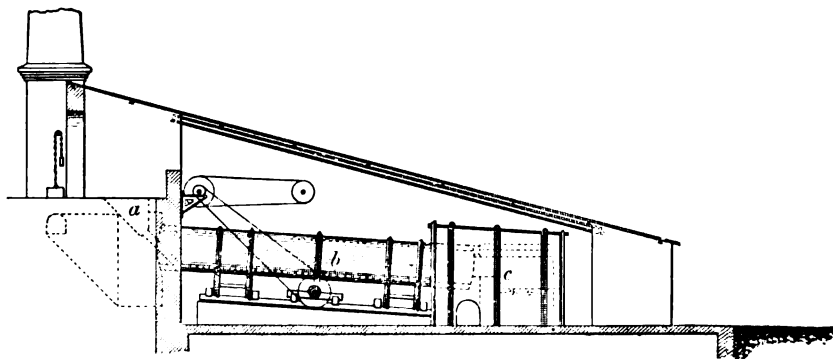


FIG. 13.

placed between two or four such furnaces, or in front of them, whilst in the latter case they are built above them. The reverberatory furnaces are composed of flat brick arches over hearths of varying shape and size. A calcining furnace combined with a Belgian zinc-reduction furnace, such as was formerly in use at Moresnet, is shown in Figs. 14 and 15. The products of combustion from the reduction furnaces enter the furnace body *h* through the slot *k*, and escape from the former through the flue *f* into a stack 23 feet in height. The ores are charged into the furnace through an opening *z* in the crown of the arch. The burnt ores are discharged through a vertical flue *w* into a vault *g* built below the furnace. At *p* there are working doors

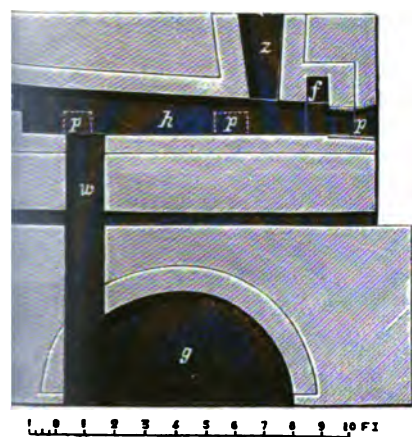


FIG. 14.

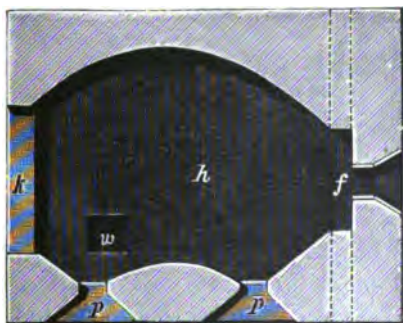


FIG. 15.

through which the ores in the furnace can be rabbled. A furnace of this kind will calcine from 36 cwt. to 2 tons of calamine in 24 hours.

Calcining furnaces attached to Silesian smelting furnaces have areas of from 10 to 53 square feet, and are connected with both the older and some of the newer forms of these furnaces. They have, however, an injurious effect upon the output of zinc both by reason of cooling the furnace walls, as also by interfering with the draught, and have, therefore, been entirely discarded in the most recent furnaces, or have been erected at some distance from them. The calcining furnaces attached to the various types of Silesian furnaces will be found shown in the illustrations of the latter. Both crushed calamine and lump ore can be burnt in these furnaces.

The calciners of the older Silesian furnaces have an area of 53 square feet. In these 1.5 tons of calamine are burned in 12 hours,

In the calciners of the draught-fired furnaces, which have an area of 10 square feet,  $8\frac{1}{2}$  cwts. of calamine can be roasted in 8 hours. In the calciners of the blast-fired furnaces, which have an area of 168 square feet, 14 cwts. can be burned in 8 hours.

At Lipine, where reduction furnaces fired with gas and provided with heating shafts are used, a small calciner is placed on either side in the middle of the furnace block. Its length is 7 feet 3 inches, its breadth 2 feet 8 inches, and its height 2 feet 4 inches. In 24 hours, from 2 tons 5 cwts. to 3 tons of calamine can be calcined. The labour is provided by the men in charge of the reduction furnace. On the average, burnt Upper Silesian calamine retains some 17 per cent. of carbon dioxide.<sup>1</sup> Such of the latter as does not escape before the reduction of the zinc oxide, must be reduced to carbon monoxide by an excess of carbon in the muffles.

#### *(b) Calcination of Zinc Blende.*

The object of calcining zinc blende is to convert the sulphide of zinc into oxide by means of atmospheric air. Simultaneously the other sulphides contained in, or mixed with, the zinc blende are also converted into oxides. Any carbonates intermixed with the blende have also to be converted into oxides. From any arsenical and antimonial compounds that may be present, the arsenic and antimony must, moreover, be volatilised as completely as possible. The calcination must be conducted so that as little sulphur as possible remains in the calcined ore, because sulphide of zinc, whether it be present in the form of zinc blende that has remained undecomposed, or whether it is produced during the reduction process by the reduction of zinc sulphate, remains undecomposed when the zinc is reduced, so that its zinc contents are lost for the extraction of zinc. The complete removal of sulphur from the ore is, however, only exceptionally attained, because in calcination the last portion of sulphur can only be driven out with great difficulty, and because the formation of zinc sulphate, which is only completely decomposed at a red heat approaching whiteness, is unavoidable. Moreover, blende is often accompanied by substances such as galena, chalcopyrite, stibnite, and silicates of iron and manganese, which are inclined to sinter or melt at high temperatures. These envelope particles of blende and prevent the oxygen of the air from acting upon them. Under these circumstances, it is quite unavoidable that small portions of sulphur, say 1 to 2 per cent., should remain in the

<sup>1</sup> Steger, *Eisen und Metall.* p. 67, 1888.

calcined ore. To obtain as complete a calcination as possible, it is necessary that the blende should be crushed down to a mesh of 0.04 inch, or, at the outside, of 0.08 inch, and for the decomposition of the basic sulphate formed the final temperature must be proportionately high. A high temperature entails, on the other hand, the objections that zinc oxide is volatilised, that it is reduced to zinc when brought in contact with the particles of carbon in the flame, and that the ore may be sintered or fused. Zinc sulphate can only be imperfectly decomposed by mixing carbon with the calcined ore. When pulverulent zinc blende containing only sulphide of zinc is calcined, as soon as the temperature rises to a low redness the sulphur is oxidised to sulphur dioxide, and the zinc which was combined with this sulphur is converted into oxide. The sulphur dioxide is in part volatilised, in part it is converted by contact with the red-hot portions of the ore and of the furnace walls into sulphur trioxide, which latter combines with a portion of the zinc oxide to form sulphate. The lower the temperature, and the more the zinc blende is intermixed with other sulphides, the more zinc sulphate is formed. Thus in some experiments by the author, when an intimate mixture of equal parts of zinc blende and galena from the Broken Hill Mines in New South Wales was calcined at low redness, 40 per cent. of the zinc contents of the blende was converted into zinc sulphate. The formation of zinc sulphate is promoted more by the presence of pyrites than by that of any other sulphides. When the temperature is raised to a cherry-red, the neutral zinc sulphate is split up into basic zinc sulphate and to sulphur trioxide or sulphur dioxide and oxygen. By further raising the temperature to the fullest red heat, the basic zinc sulphate itself is decomposed in the same way. Schlapp found that during the decomposition of zinc vitriol dehydrated as completely as possible, by means of heat on a large scale, some 30 per cent. of the sulphur trioxide escaped as such, whilst the remainder was split up into sulphur dioxide and oxygen.

If the calcination takes place in reverberatory furnaces, any carbon monoxide present in the products of combustion has a reducing action upon the zinc oxide at the high temperature required to split up the basic zinc sulphate. The zinc vapours thus formed are carried off, and are at once oxidised again by the air and the carbon dioxide present, so that loss of zinc is thus incurred. With a sufficiently long continued calcination and the employment of a sufficiently high temperature, it is, as above shown, possible to convert the whole of the zinc sulphide into oxide. As a rule, however, in consequence of the difficulty of completely decomposing the

basic sulphate and of oxidising the last portions of the sulphide of zinc present, small quantities of sulphur remain in the ore. In a series of experiments<sup>1</sup> the following decrease in the percentage of sulphur in the ore was found on roasting three different grades of ore in a Hasenclever furnace with three muffles lying one above the other:—

PERCENTAGE OF SULPHUR IN THE ORE.

	No. 1 Ore.	No. 2 Ore.	No. 3 Ore.
Blend before charging . . . .	19.2	26.8	26.5
On leaving the first muffle . . .	17.6	19.1 -19.9	15.9 -21.4
On leaving the second muffle . .	12.0	11.2 -14.3	9.9 -12.4
On leaving the third muffle . . .	3.4	1.02- 1.48	0.75- 1.06
On drawing from the furnace . .	0.6	0.35- 1.02	—

The temperature in the first or uppermost muffle was from 580° to 690°, that of the two lower ones 750° to 900° C. If the blende contains, as is often the case, sulphide of iron isomorphously intermixed, magnetic oxide and iron sulphate are at first produced. As the temperature increases, the magnetic oxide is converted into ferric oxide, whilst the sulphate of iron is converted into sulphur dioxide and oxygen and basic sulphate of iron, which last, when the temperature rises still further, is ultimately split up into ferric oxide and sulphur trioxide, or in part into sulphur dioxide and oxygen. This decomposition takes place far below the temperature of decomposition of zinc sulphate, and the gases produced by the splitting up of the sulphate of iron promote the conversion of sulphide of zinc into sulphate. At the conclusion of the operation, all the sulphide of iron will have been converted into ferric oxide, so that the product will consist of a mixture of ferric oxide and zinc oxide, together with small quantities of zinc sulphate and undecomposed sulphide. Prost's<sup>2</sup> experiments indicate that the compound  $\text{ZnFe}_2\text{O}_4$  is formed when oxides of iron and zinc are heated together. According to Jensch,<sup>3</sup> the sulphur contained in dead roasted zinc blende in the form of sulphide is said to be exclusively combined with iron. A calcination down to 0.5 per cent. of sulphur, present in the form of sulphide, would thus appear to be possible only in the case of blende free from or very poor in iron. In spite, however, of careful dressing operations, blende is frequently intermixed with pyrites, chalcopyrite, galena, stibnite, arsenides and sulph-arsenides, spathic iron ore.

<sup>1</sup> *Fischer's Jahresber.* 1890, p. 444.

<sup>2</sup> *The Mineral Industry*, p. 596, 1896.

<sup>3</sup> *Zeitschr. angew. Chem.* 1894, p. 50.



barytes, quartz, calcspar, dolomite and various silicates. It also often contains silver in extractable quantity.

*Pyrites* is converted into ferric oxide by calcination. In consequence of its ready oxidisability, it promotes the commencement of calcination and the raising of the ore to a red-heat, but at the same time causes the formation of considerable quantities of sulphate of zinc. If sulphide of iron remains undecomposed after the calcination, it has an injurious effect in the process of reduction, as it perforates the walls of the vessels employed. In the presence of quartz, ferrous silicate may readily be formed in consequence of the action of reducing gases or of soot upon the ferric oxide at the high temperature of calcination. This not only envelopes particles of blende, but also acts injuriously upon the walls of the vessels employed in distillation owing to the formation of readily fusible double silicates.

*Chalcopyrite* is converted on calcination into a mixture of cupric and ferric oxides, and has the same disadvantages as iron pyrites. The cupric sulphate formed by its calcination decomposes at a far lower temperature than basic zinc sulphate. As this ore is greatly inclined to sinter on account of its containing sulphide of copper, it is very apt to envelope particles of unroasted zinc blende if the temperature is at all high at the outset.

*Galena* is converted into a mixture of oxide and sulphate of lead; as it sinters very rapidly, it is also apt to envelope particles of zinc blende, unless the temperature is kept very low at the outset. It also promotes the formation of zinc sulphate by the action of sulphur dioxide and oxygen or of sulphur trioxide upon zinc oxide or sulphide. Any lead sulphate which is not decomposed at the temperature of calcination melts just as lead oxide does at the temperature required to decompose zinc sulphate, and both substances are apt to envelope particles of the ore. In the presence of quartz, silicate of lead forms, which is also easily fusible, and envelopes particles of ore. Lead oxide, as long as it is not present in too great a quantity (under 8 per cent.), is reduced in the process of reduction to metallic lead, provided that the gases of the vessels contain carbon monoxide. The lead thus formed partly volatilises with the zinc and partly remains in the residue. When it is present in large quantities, and if oxidising gases or air are present in the vessels employed in distillation, it is partly converted into silicate of lead. This silicate of lead gives rise to the formation of readily fusible silicates, and thus rapidly destroys the walls of the vessels. At the same time, lead may be reduced from it, and alloy

with the zinc. In the experiments of Sander<sup>1</sup> at Prayon-Trooz, zinc blende, containing 6 to 11 per cent. of lead, lost on roasting 7.88 to 21.8 per cent. of its lead.

*Stibnite* sinters very rapidly, and envelopes particles of uncalcined zinc blende. Its sulphur is converted into sulphur dioxide and promotes the formation of zinc sulphate. The antimony is converted into oxide, which partly volatilises and partly forms antimoniates. The latter are also formed in part by the action of the oxide of antimony upon sulphates. These antimoniates remain for the most part undecomposed during calcination, and therefore appear as such in the calcined ore.

*Arsenides* and sulph-arsenides give off their sulphur as sulphur dioxide, and a portion of the arsenic forms arsenic acid; another portion of the arsenic forms arseniates of those metals (nickel, cobalt, iron and silver) whose arseniates resist the heat. The ultimate product of the calcination consists, therefore, of a mixture of metallic oxides and arseniates. During the process of reduction, the latter are reduced, yielding metallic arsenic, which passes into the zinc.

*Siderite* is converted on calcination into magnetic oxide, which promotes the formation of readily fusible silicates during the process of reduction, and, thereby, the destruction of the vessels employed. If quartz is simultaneously present in the ore, a readily fusible silicate of iron may form even during calcination, which would envelope portions of the ore. If the spathic ore contains manganese very fusible double silicates are apt to be formed, in consequence of the ready fusibility of silicate of manganese.

*Quartz* by itself has no injurious effect on calcination, as it only combines with zinc oxide at a white heat. It may, however, give rise to readily fusible silicates when pyrites, chalcoppyrite or siderite are present in the ore.

*Barytes* remains unchanged during calcination. In the process of reduction it becomes reduced to barium sulphide, which is variously stated to promote<sup>2</sup> and to have no influence<sup>3</sup> on the formation of zinc sulphide.

*Calcite* is converted partly into lime and partly into calcium sulphate. Lime, together with ferrous oxide, forms readily fusible double silicates with the silica of the containing vessels, and these silicates are apt to destroy the walls of the latter. The calcium

<sup>1</sup> *Berg- und Hüttenm. Ztg.* p. 562, 1902.

<sup>2</sup> Sander, *ibid.* 1902, p. 466.

<sup>3</sup> Thum, *Berg- und Hüttenm. Ztg.* 1876, p. 154.

sulphate is reduced to sulphide during the reduction of the zinc oxide, and thus gives rise to the formation of residues rich in zinc. Thum<sup>1</sup> states that the sulphides of the alkaline earths appear to give up half of their sulphur to zinc in the presence of free zinc and carbon. Other authorities<sup>2</sup> state that the presence of calcium sulphate in the distillation charge produces no loss of zinc.

*Dolomite* behaves like calcite.

*Argentite* is converted into sulphate of silver, which, in the last stage of calcination, becomes decomposed into silver, sulphur dioxide and oxygen. A portion of the silver is volatilised in the last stage of the calcination at the high temperature then prevailing. According to Sander,<sup>3</sup> zinc blende containing 340 to 375 grains of silver per ton lost 10 to 12 per cent. of its silver on roasting.

If readily fusible silicates, especially those of iron and manganese, are mixed with zinc blende, these will sinter in the last stage of the calcination, and envelope particles of ore.

The loss of weight, by calcination, of zinc blende varies with its impurities and with the temperature, ranging between 12 and 20 per cent. The completeness of the removal of sulphur from the crushed and roasted zinc blende when the calcination takes place in reverberatory furnaces or muffles, may be proved by the chlorate of potash test or by hydrochloric acid. The amount of sulphur in the form of sulphates, however, can only be determined gravimetrically or by titration with barium chloride.

The chlorate of potash test, which is considered the most convenient, is executed by heating an iron spoon to redness in the furnace, and melting some 30 grains of chlorate of potash in it. Upon the molten salt a small quantity of the ore to be examined is then sprinkled. If no sparks are produced, due to the presence of burning sulphur, calcination is complete. Even the presence of only a few small sparks is considered the sign of a good calcination, because in this case the sulphur has been removed down to 1 per cent. The hydrochloric acid test consists in heating a small quantity of the ore with pure zinc and dilute hydrochloric acid in a test-tube. When sulphur is present in the ore, sulphuretted hydrogen is evolved. The quantity of the latter, and, therefore, that of the sulphur present in the ore, is determined by means of a strip of paper soaked in acetate of lead, which takes a colour varying from light to dark brown, according to the quantity of sulphur present. The percentage of sulphur may be estimated by this test to between a half and one-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Berg- und Hüttenm. Ztg.* p. 562, 1902.

<sup>3</sup> *Zeitschr. angew. Chem.* 15, p. 353, 1902.

quarter per cent. The colours obtained may be compared with colours which have been produced by roasted blende of known sulphur content, provided always that the tests are executed in the same manner.

### *The Process of Calcination*

Blende can only be calcined satisfactorily in reverberatory furnaces and muffle furnaces. Calcination in heaps, stalls and shaft furnaces is only available for rendering the ore friable, or for a preliminary roasting. Calcination in such apparatus must, accordingly, be followed by calcination in reverberatory or muffle furnaces. Reverberatory furnaces produce gases which contain sulphur dioxide intermixed and highly diluted with the products of combustion, so that the sulphur dioxide cannot be utilised; such furnaces should, therefore, be used only when the utilisation of the products of calcination for the production of sulphuric acid is impracticable, on account of the absence of a market, and when the gases emitted may either be allowed to escape in the neighbourhood of the smelting works, or when they can be rendered innocuous by processes which do not cause too great an outlay. Muffle furnaces admit of as good a calcination of zinc blende as do reverberatory furnaces, and do not require much more fuel than the latter, if proper use is made of the heat developed by the oxidation of the sulphide of zinc. As these furnaces produce gases containing so much sulphur dioxide as to be suitable for the manufacture of sulphuric acid, they should be employed, as a rule, when there is a market for sulphuric acid in the neighbourhood of the works, or when the sulphur dioxide can be utilised with advantage in some other way. Before the introduction of the newer forms of muffle furnace, muffle furnaces combined with reverberatory furnaces were also used. In the muffles of these combined furnaces, sulphur dioxide was produced for the purpose of sulphuric acid manufacture, whilst the blende was roasted dead upon the hearths of the reverberatory furnaces. Their erection may be justified when there is only a limited market for sulphuric acid, so that only a portion of the sulphur dioxide contained in the gases can be worked up with advantage. Heaps and stalls can only be employed for rendering very compact blende more friable in such districts in which it is impossible to utilise the sulphur dioxide, and in which no injury is inflicted by the latter on the neighbourhood. In such cases, the calcination should be looked upon as a preliminary to the crushing of the lump ore, which has to be calcined dead in reverberatories after it has been crushed.

Shaft furnaces may be used for preliminary roasting with certain varieties of blende which burn readily, when it is only possible to utilise the gases produced to a limited extent. After this preliminary calcination, the lump ore has to be crushed and roasted dead in reverberatory furnaces, whilst blende that has been partly roasted in the form of powder goes direct to the reverberatory. If, on the other hand, it is possible to utilise the whole of the sulphur dioxide available in the calcination of the blende, calcination in muffles is to be preferred to the combined calcination in shaft and reverberatory furnaces, as the former type of furnace also admits of the utilisation of the heat developed by the oxidation of the sulphide.

We have, therefore, to consider :—

Calcination in heaps and stalls.

Calcination in shaft furnaces.

Calcination in reverberatory furnaces.

Calcination in combined reverberatory and muffle furnaces.

Calcination in muffle furnaces.

### *Calcination in Heaps and Stalls*

This process can only be employed exceptionally for calcining blende in order to render it friable in districts in which no complaints are to be feared on the score of the sulphur dioxide vapours, as was the case, for instance, at the mines of the Lehigh Company of Bethlehem in Pennsylvania.<sup>1</sup> At these mines lump ore was calcined, resting upon a grate of iron bars supported by two outer walls and one central wall, in heaps 28 feet in length, 15 feet in width, and 8 feet 2 inches high, a wood fire being applied below the grate. The calcined blende was crushed and then roasted dead in reverberatory furnaces. The employment of stalls is unknown to the author. Neither of the above modes of calcination is probably in use at the present day.

### *Calcination in Shaft Furnaces*

Shaft furnaces are employed for the preliminary roasting of lump ore or of concentrates. In both cases the sulphur dioxide that escapes during this preliminary roasting is to be utilised for sulphuric acid manufacture. The partly roasted ores are then completely desulphurised in reverberatory furnaces without any attempt being made to utilise the sulphur dioxide that escapes in this further

<sup>1</sup> *Berg- und Hüttenm. Ztg.* 1872, pp. 53–61.

roasting. Lump blende may be part roasted in kilns or pyrites burners; for the preliminary roasting of pulverulent blende the Gerstenhöfer furnace has come into use.

### *Calcination of Lump Blende in Shaft Furnaces*

Kilns or pyrites burners may be employed for roasting blende in lumps.

Kilns are moderately high shaft furnaces, in which the ore to be roasted rests either upon a grate or upon a flat or saddle-shaped floor.<sup>1</sup> They are distinguished from pyrites burners by their greater height (4 feet 9 inches to 6 feet 9 inches), and they keep the temperature better together than the latter. They are, therefore, specially suitable for the calcination of blendes which are low in pyrites and in sulphur. The shaft of these kilns is rectangular or square in cross section, 3 feet 3 inches to 5 feet wide in the clear, and 5 feet to 8 feet 3 inches long in the clear. As soon as the blende has taken fire, it continues to burn by itself on account of the heat generated by the oxidation of its constituents, and this produces the temperature requisite to maintain the calcination. In favourable cases the sulphur may be removed down to 6 to 8 per cent. Upon the average, the quantity of ore put through in one shaft amounts to 1 ton per 24 hours. In the Freiberg kilns, whose construction has been described in Vol. I., p. 53, 1·2 tons of blende are roasted in 24 hours, from 30 per cent. of sulphur down to 8 per cent., calcined ore being drawn four times. This ore is then ground and calcined in reverberatory furnaces down to 1 per cent. of sulphur.

Pyrites burners are low-shaft furnaces in which the ores to be roasted lie upon a grate of movable bars. These have been described and illustrated in Vol. I., p. 47 *et seq.* They are suitable for the preliminary calcination of easily combustible blendes, and will treat smaller pieces (down to walnut size) than will kilns. The sulphur may be brought down to 6 to 8 per cent. At Letmathe, near Iserlohn,<sup>2</sup> pyrites burners were employed, 6 feet 3 inches to 6 feet 6 inches in length and width, and 4 feet 3 inches to 4 feet 5 inches high, each with one working door in either of the free sides, several such furnaces being built together in a block. Each shaft roasted 1 ton of zinc blende in 24 hours down to 7 per cent. of sulphur. The roasted ore was then roasted dead in reverberatory furnaces.

At Lipine, pyrites burners were in use in 1895 the height of which above the floor of the works is 9 feet 2 inches; the shaft is

<sup>1</sup> Vol. I. p. 53.

<sup>2</sup> Kerl, *Metallhüttenkunde*, p. 439.

4 feet 1 inch square. Twenty-six furnaces form a block. The height of the layer of blende above the grate amounts to 16 inches. In 24 hours half a ton of blende, containing 25 per cent. of sulphur, is roasted down to 10 per cent. The gases evolved contain 6 per cent. by volume of sulphur dioxide. One attendant is required to every 10 furnaces, working a 12-hour shift. The roasted blende is crushed in rolls and then roasted dead in reverberatory furnaces.

At the Recke Works, near Rosdzin, in Upper Silesia, pyrites burners were in use in 1895, the shaft being 3 feet 3 inches wide and deep, with a total height of 8 feet 2 inches. The blende is broken to nut size, and contains 24 to 33 per cent. of sulphur. The height of the layer above the grate amounts to 2 feet. In 24 hours, 7 cwts. of blende are roasted in each shaft down to 7 per cent. of sulphur; the escaping gases contain 7 per cent. by volume of sulphur dioxide. There are 23 to 30 such shafts combined to form one block; each such block requires two attendants with two assistants per day. The calcined ore is ground between rolls and then roasted dead in long-bedded calciners. The output of a set of rolls is 100 tons in 12 hours.

#### *Calcination of Crushed Blende in Shaft Furnaces*

As far as the author knows, Gerstenhöfer furnaces are the only ones of this class that have come into use up to the present for calcining pulverulent blende. These furnaces, which are specially adapted for pyritic blende, have been described and illustrated in Vol. I., p. 56. If the result is to be satisfactory, the blende must be crushed very small, entailing, however, the objection of the formation of a considerable quantity of flue-dust. Even in the most favourable conditions, the sulphur can nevertheless not be brought down below 5 or 6 per cent., so that even here a subsequent calcination in reverberatory furnaces is necessary; the Gerstenhöfer furnace can also be used for this after-calcination by converting the lower part of it into a kind of reverberatory furnace by means of a lateral fireplace. In this case the escaping gases cannot be utilised in the manufacture of sulphuric acid, so that the employment of a long-bedded furnace for the dead roasting of the blende is preferable; the arrangement of a Gerstenhöfer furnace combined with an auxiliary fireplace is shown in Fig. 16. *T* is the lower part of the shaft with the carriers *t* for the ore; *F* is the fire-grate from which the products of combustion pass through the flue *c* into the shaft. *H* is a portion of the dust chamber; *s* is a screw for the conveyance of the calcined ore into the waggon *w*;

*k* is a flue which conveys the sulphur dioxide escaping from the residues into the stack. In the Gerstenhöfer furnace 1 to 2 tons of blende can be roasted in 24 hours. It has the objection that a very considerable amount of flue-dust is produced, and for this reason has only been definitely employed in a small number of works. It has

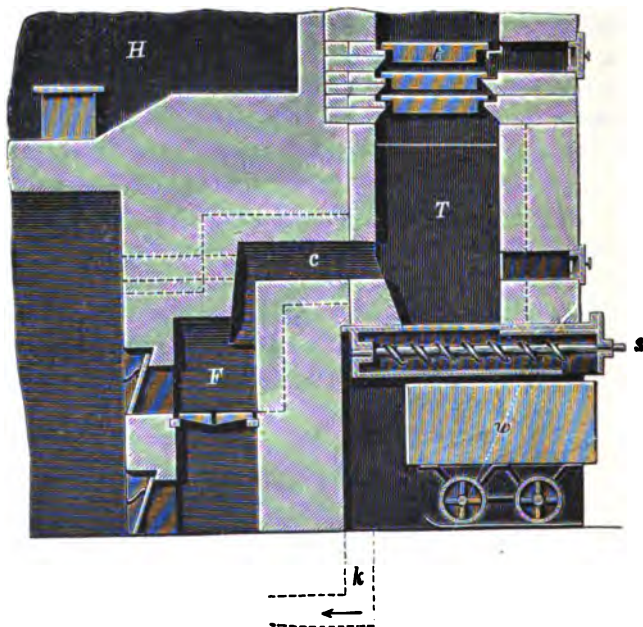


FIG. 16.

- been used for calcining blende at the Mulden works, near Freiberg and at Swansea, in England.

### *Calcination in Reverberatory Furnaces*

Reverberatory furnaces should, as a rule, be employed for the calcination of zinc blende when the gases produced are not to be utilised. In cultivated countries the sulphur dioxide formed in these furnaces can only be allowed to escape into the air in a highly dilute condition, or else it has first to be rendered innocuous. Reverberatory furnaces admit of a rapid and complete calcination and require less fuel and labour than muffle furnaces. Of grate-fired reverberatories, only that of Spirek (p. 31) has come into use for the calcination of calamine. Nothing is known as to its efficiency in roasting blende; nor has it yet been established whether the



Stetefeldt furnace (which gives such good results as regards fuel consumption, capacity and attendance in the chloridising roasting of silver ores) is suitable for roasting zinc blende. The rabbling and stirring of the crushed ore requisite for a good calcination may be performed either by hand-work or mechanically. The working chamber of the reverberatory furnace is either fixed or else movable. In the latter case, the hearth alone may either be rotated or else the whole working chamber may be movable. We, therefore, have to distinguish between—

Fixed Reverberatory Furnaces.

Reverberatory Furnaces with Movable Hearths.

Reverberatory Furnaces with Movable Working Chambers (rotating cylinders).

Solid fuels are generally employed, though in Jola in the United States natural gas is used with conspicuous success both for mechanical and hand-worked furnaces.

#### *Calcination in Fixed Reverberatory Furnaces*

Fixed reverberatory furnaces may be divided into those worked by hand and those worked by machinery. The latter kind should be employed in districts where the cost of labour is high, whereas where labour is cheap the former class should have the preference both over the latter types, as also over reverberatory furnaces with movable hearths or working chambers.

#### *Calcination in Fixed Reverberatories worked by Hand*

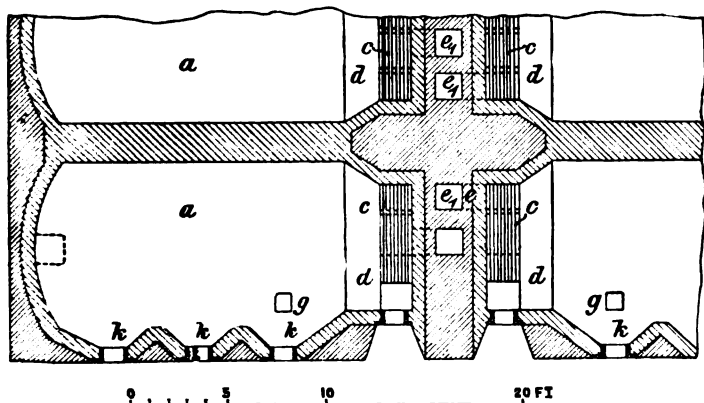
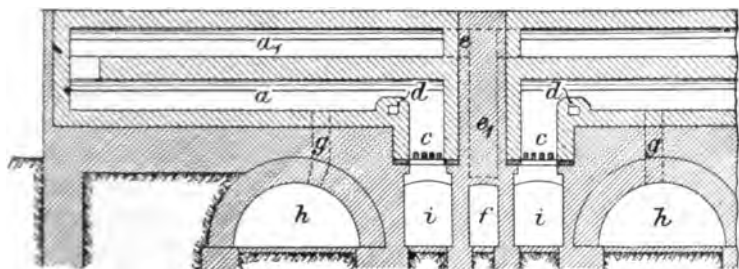
It is only in rare cases that such furnaces are heated by the waste heat from zinc reduction furnaces. Such an employment of waste heat cannot be recommended, seeing how much care is required in the calcination of zinc blende, and seeing that the temperature which the various stages of this roasting require has to be carefully graduated. As a rule, therefore, the calcination of zinc blende should be carried on independently of the reduction furnaces.

#### *Independent Reverberatory Furnaces worked by Hand*

These furnaces are best built as long-bedded furnaces working continuously (*Fortschauflungsöfen*). Smaller furnaces working intermittently, in which the whole charge is fed in at once and withdrawn similarly, are not to be recommended owing to their small output and

high cost for labour and fuel. Such furnaces have probably passed entirely out of use. The long-bedded furnaces are best fitted with only one hearth, these presenting the advantages, as compared to those with several hearths, one above the other, of smaller first cost, less need for repairs, and greater facility in working and charging; the latter kind should only be used where ground space is either very valuable or not obtainable. The heat economised by several hearths is not of any importance. It may also be saved with furnaces having but one hearth, if the products of combustion are carried off through arched flues disposed under the hearth, and if the furnace itself is coated with a non-conductor of heat. In spite of the above objections furnaces with two hearths have up to the present received the preference over those with one hearth. The length of the hearth depends upon the sulphur contents of the blende. As the sulphur acts as fuel, the hearth may be longer the greater the percentage of sulphur in the blende. Experience has shown that with single hearth furnaces the hearth should not exceed 40 feet, and that with two hearths placed one above the other the sum of the two hearths should not be greater than 50 feet. A greater length than the above is not beneficial as regards the result of the calcination; it increases the first cost and requires more labour. The width of the hearth must be such that the ore can readily be rabbled and pushed on. If the furnace only possesses working doors in one of its long sides, which seems to be an advantage in the calcination of blende in order not to dissipate heat, its width must not greatly exceed 8 feet. If, on the contrary, it has working doors on both of its long sides, the width of the hearth may be increased up to 13 feet. Such furnaces are, however, only employed exceptionally, because a uniform calcination is more difficult in them, and the consumption of fuel is increased. The number of working doors must be kept as low as possible, as the furnace is cooled by them. In order to economise heat, it is, therefore, usual to have the working doors in one side only, in spite of the greater difficulties in working. Experience has shown that the distance between the centre lines of two adjacent working doors should not exceed 8 feet, for the sake of convenience in working. The projections between the working doors must also be kept as small as possible. The distance between the hearth and the arch of the roof should not greatly exceed 18 inches. To utilise the heat to the best advantage, it is usual to incline the arch of the roof downwards, or to allow the hearth to rise either uniformly or stepwise, towards the flue-bridge. As very high temperatures are not required for calcination, an ordinary grate-fire is generally employed.

gas-firing is only made use of when inferior fuels, or fuel that will not give a long flame, are alone available. The construction of such a long-bedded calciner for the calcination of zinc blende does not differ, except as regards dimensions, from the furnace described and illustrated in Vol. I., p. 76. In a single-hearth calciner 40 feet in length, 8 to 10 feet wide, with a grate 6 feet 6 inches long and 18 inches wide, 3 tons of zinc blende can be roasted in 24 hours with a consumption of 1 ton of coals, and with one man per shift.<sup>1</sup> The ore is introduced



FIGS. 17 and 18.

in charges of 15 cwts. through an opening in the roof of the flue, and is pushed forward at intervals of 6 hours. Accordingly, there are four charges of ore in the furnace at once, and 15 cwts. are drawn every 6 hours. The ore is rabbled in 15-minute intervals.

Long-bedded calciners with several hearths usually possess two of the latter; more than two are only used exceptionally. The construction of such a double-hearth furnace is shown in Figs. 17 and 18.<sup>2</sup> Four such furnaces are built together to form a block; *c* is the grate,

<sup>1</sup> Thum, *op. cit.* p. 202.

<sup>2</sup> *Berg- und Hüttenm. Ztg.* 1877, p. 100.

lying 2 feet 4 inches below the fire-bridge  $d$ , which is hollow and cooled by an air flue;  $a$  is the lower hearth,  $a_1$  the upper hearth, the length of each being 15 feet 3 inches, and their clear width 8 feet;  $e$  is the flue through which the products of combustion escape into the condensing flues  $e_1$ , and thence to the flue  $f$ , leading to the stack. To each block of four furnaces there is one stack;  $i$  is the ashpit,  $k, k$  are the working doors,  $g$  is an opening closed during calcination, through which the calcined blende can be dropped into the vault. In such a furnace 3 to 4 tons of blende are roasted in 24 hours, with one man on each shift, and with a consumption of 30 per cent. of fuel. These furnaces have been generally replaced by muffle furnaces, since the latter allow of the utilisation of the furnace gases. They have been used at the zinc works in Upper Silesia, Westphalia and Belgium. In these from  $2\frac{1}{2}$  to 6 tons of ore, according to the size of the furnace, are put through, with a consumption of from 25 to 40 per cent. of coal, according to the quality. For the smaller furnaces treating up to 3 tons, one workman per shift is enough; for the larger furnaces two men are required.

At Oberhausen<sup>1</sup> the furnace hearths are each 21 feet 4 inches long and 6 feet 6 inches wide. The cross section of the grate is 6 feet 6 inches by 1 foot 4 inches. In 24 hours, 3 tons of ore are put through, with a consumption of 12 to 14 cwts. of small bituminous coal, containing 11 per cent. of ash. The calcined ores contain 0.57 to 0.83 per cent. of sulphur. The loss of zinc during calcination does not exceed 0.75 per cent. At Ammeberg,<sup>2</sup> in Sweden, similarly constructed furnaces are used, fired by gas. In 24 hours, 3 tons 2 cwts. of blende are calcined down to 1.20 to 1.25 per cent. of sulphur, with a consumption of 11 cwts. of small coal. Four furnaces are worked by a staff of 20 men in two 12-hour shifts. At Münsterbusch, near Stahlberg, a furnace with hearths 20 feet 7 inches in length and 9 feet 3 inches in width, having 5 working doors along one side, calcined  $2\frac{1}{2}$  tons of blende per 24 hours in 4 charges, with a consumption of 39 cubic feet of coal. Every 6 hours a charge of ore was drawn from the furnace, and a new charge was put in. Three hours after each charging, all the ore contained in the furnace was thoroughly rabbled. At the Hohenlohe Works, near Katowitz, in Upper Silesia, there are double-bedded furnaces, with 5 working doors along one of the longer sides. Three charges of 1 ton each are contained simultaneously in the furnace, two on the upper and one on the lower hearth. Each charge remains for 5 hours before it is moved forward, so that the ore remains altogether 15 hours in the furnace. Every 5 hours a

<sup>1</sup> Mahler, *Annales des Mines*, vol. vii, book iii, p. 152, 1885.

<sup>2</sup> *Ibid.*

charge is drawn from the furnace, and a new charge introduced upon the upper hearth. In 24 hours some 5 tons of blende are calcined down to 1 per cent. of sulphur in one such furnace, with a fuel consumption amounting to 25 per cent. of the weight of the raw ore. The escaping gases contain 1 per cent. by volume of sulphur dioxide. For the absorption of the latter they are made to pass upwards and downwards through towers containing milk of lime, and finally discharged into a stack 328 feet high. At the Silesian Works, near Lipine, double-hearth calciners were in use. The length of the hearths amounted to 22 feet, the width to 6 feet 6 inches. There were 4 to 5 working doors to each hearth. The furnace contained 3 charges of 13 cwts. each at one time. In 24 hours a furnace put through 5 tons 2 cwts. of blende, with a consumption of 24 cwts. of inferior coal. The labour employed in the 12-hour shift amounted to 2½ men, two of whom looked after the calcining and the firing; a labourer, working a quarter shift, looked to the charging of the blende and wheeled in the coals. At the Recke works, near Rosdzin, double-hearth calciners were in use, the length of each hearth being 20 feet. The width amounted to 6 feet 6 inches, with six working doors to each hearth. In 24 hours, 3½ tons of blende were calcined, with a consumption of 1 ton of small coal. One man worked the furnace on a 12-hour shift. At the Cilli<sup>1</sup> works a part of the blende, poor in sulphur, is calcined in double-hearth furnaces, each hearth being 25 feet long and 8 feet broad, with working doors along one of the longer sides. In 24 hours 3 charges of 15 cwts. each are roasted.

The decrease in the sulphur and the formation of zinc sulphate during the calcination of blende in a double-bedded calciner at the works of the Vieille Montagne, near Flône, in Belgium, are shown in the following table, in which A designates uncalcined ore, Z calcined ore, 2 to 8 the various samples taken one after another:—

Sample.	Zinc sulphide per cent.	Zinc sulphate per cent.	Zinc oxide per cent.
A . . . . .	83.0	0	0
2 . . . . .	70.5	3.7	15.2
3 . . . . .	52.2	3.9	34.6
4 . . . . .	51.5	4.2	38.0
5 . . . . .	43.0	11.0	41.5
6 . . . . .	23.2	12.3	57.8
7 . . . . .	17.7	7.8	65.0
8 . . . . .	8.6	6.2	75.5
Z . . . . .	1.9	5.9	81.0

<sup>1</sup> *Berg- und Hüttenm., Ztg.* No. 4, 1894.

A similar comparison of the results of calcining blende in a single-hearth reverberatory furnace at the works of the Austro-Belgian Company at Corphalie, in Belgium, is as follows :—

Sample.	Zinc sulphide per cent.	Zinc sulphate per cent.	Zinc oxide per cent.
A . . . .	64.5	0	0
2 . . . .	58.0	3.4	4.6
3 . . . .	38.0	7.9	19.0
4 . . . .	17.5	8.4	39.0
5 . . . .	10.0	2.6	50.5
Z . . . .	1.2	2.2	59.7

Multiple-hearth furnaces were used at La Salle in the State of Illinois, United States of America.<sup>1</sup> The separate hearths form shelves placed alternately one above the other, as in the Malettra furnace (Vol. I., page 66), over which the ore passes from top to bottom, whilst the flames and products of combustion travel in the opposite direction. The furnace forms a cube of 15 feet side and is composed of 5 separate divisions lying side by side, each 3 feet wide and 15 feet long. Each of these divisions has 8 hearths one above the other, as described. Each furnace of 5 compartments puts through 36 cwts. of blende in 24 hours. Recently the muffle furnaces, hereafter to be described, have been employed at La Salle.

*Reverberatory Furnaces heated by the Waste Heat of Zinc Reduction  
Furnaces and worked by Hand*

Such furnaces have been constructed by Thum in England, where they were heated by the waste heat of a Belgian zinc furnace. Such a furnace with a hearth 41 feet long and 10 feet broad, the height of the arch above the hearth being 2 feet, was in operation at Bagillt, and calcined 30 to 32 cwts. of blende in 24 hours. These furnaces are open to the serious objection that the calcination is entirely dependent upon the working of the reduction furnaces, and are, therefore, not to be recommended. Waste heat from the reduction furnace can be employed more advantageously for other purposes.

*Calcination in Fixed Reverberatory Furnaces worked by Machinery*

The furnaces belonging to this class are furnaces with movable rabblers for stirring the blende. As the movable portions are

<sup>1</sup> Leob, *Jahrb.* vol. xxvii. p. 316, 1879.

continually in need of repair and occasion no inconsiderable expense, such furnaces can only be employed with advantage in districts where wages are high. These furnaces are used particularly in the United States. Experimentally, a furnace of this kind—that of Ross and Welter—was employed at Oberhausen.<sup>1</sup> This furnace consists of three hearths, one above the other, of which the lowest is straight like that of a long-bedded calciner, whilst the two upper hearths are circular; in the two upper hearths rabble-arms, attached to a vertical shaft, are rotated as in Parkes's furnace (Vol. I., page 92). There is a charging apparatus which delivers the ore to the top-most hearth, and by means of the revolving rabbles, which make one revolution per minute, it is stirred and gradually transferred to the lower hearth. It is here again stirred by the rabble revolving once per minute, and gradually pushed on to the bottom hearth,

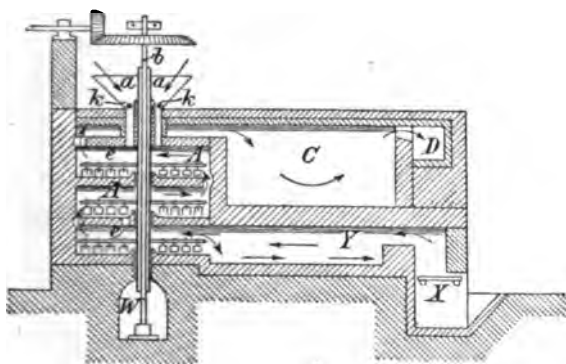


FIG. 19.

where it is rabbled and advanced by hand. The rabbles are secured to a sleeve, through which passes a vertical hollow cast-iron shaft. The latter is moved by gearing, and thus sets the sleeve in motion; air is made to pass through the hollow shaft in order to cool it. In this furnace, which is worked by one man, 3 tons of blende are said to be put through in 24 hours, with a consumption of 15 cwts. of coal. This furnace would appear to be identical with one patented by the Vieille Montagne Company,<sup>2</sup> except that the latter has three round hearths. The construction of the patented furnace is shown in Fig. 19. *A, A* are the three round hearths situated one below the other, *Y* is the rectangular hearth, *X* is the fire-grate. The products of combustion first pass over the hearth *Y*, and then over the round hearths one after the other, as shown in the figure by the arrows. From the

<sup>1</sup> Mahler, *Berg- und Hüttenm. Ztg.* p. 180, 1886.

<sup>2</sup> Ger. Pat. No. 24155.

topmost hearths they pass to the dust chamber *C*, and from the latter to the flue *D*. The ore is charged by means of a hopper *a*, and delivered by means of grooved rollers on to the topmost hearth of the furnace, whence it is gradually transferred by means of the rabblers to the lower hearths, and ultimately on to the rectangular hearth, where it is worked by hand, and finally drawn off in the calcined state. The shaft *b* of the rabblers is surrounded by a cast-iron cylinder, which is so attached to the shaft that it rotates with it; air enters the hollow space between the shaft and the cylinder from the flue *W*, in order to cool the shaft, and escapes at its upper portion situated outside the furnace. A hollow shaft could also be employed (as in the furnace of Ross and Welter), the rabble arms being attached to a sleeve consisting of two halves; this sleeve is secured to the shaft or to the cast-iron cylinder. On each bed there are two rabble-arms, *e*, secured to the shaft; the one is provided with tines placed radially, whilst inclined blades are attached to the other. The teeth rabble the ore, whilst the inclined blades of the other arms push it, according to their direction, either towards the middle or towards the circumference of the hearth, where it passes through suitably disposed openings on to the hearth below.

The furnaces of Ropp, Wethey, Pearce and Brown are used in the United States.

Pearce's furnace is represented in Figs. 20—28. *A* is the hearth with a wedge-shaped piece removed at *B* for the discharge of the roasted ore. Beneath the hearth runs the dust-chamber *C*, through which the gases pass in the opposite direction to that which they take on the hearth. *D* and *E* are the two fireplaces, from which the flames pass over a protecting arch into the hearth, and thence, together with the products of calcination, through a descending flue into the dust-chamber. Figs. 24 and 25 show the slot in the inner wall, through which the rabble-arms *H* (Figs. 20 and 21) project. These are attached to the hollow hub *J*, which is carried on a hollow stationary central column. Through it air is conveyed into the hollow hub, and thence through the hollow rabble-arms *H*. The upper portion of the inner wall is hung (Figs. 20, 21) to 8 iron I-shaped girders *K* by means of the stirrups *k* and the cross-beams *L*. The rabble-arms are braced by means of tie-rods *h*. They are set in motion by spur gearing, the larger spur-wheel being kept in its position by the rollers (Fig. 20). The weight of the rabble-arms and of the spur gearing is taken by conical rollers running on a circular track, so that there is no load on the hub *J* (Figs. 20 and 21). The driving shaft *p* traversing the dust-chamber *C* is protected



by means of a 5-inch iron pipe *P*. The blast enters the central column through the blast pipe *R*, whence it traverses the hollow hub *J* and the tubular rabble-arms *H*; the latter are furnished with openings and short pipes (Fig. 22) through which the blast streams out into the hearth. It thus cools the portions of the rabble-arms exposed to the heat and on escaping into the hearth also the plough

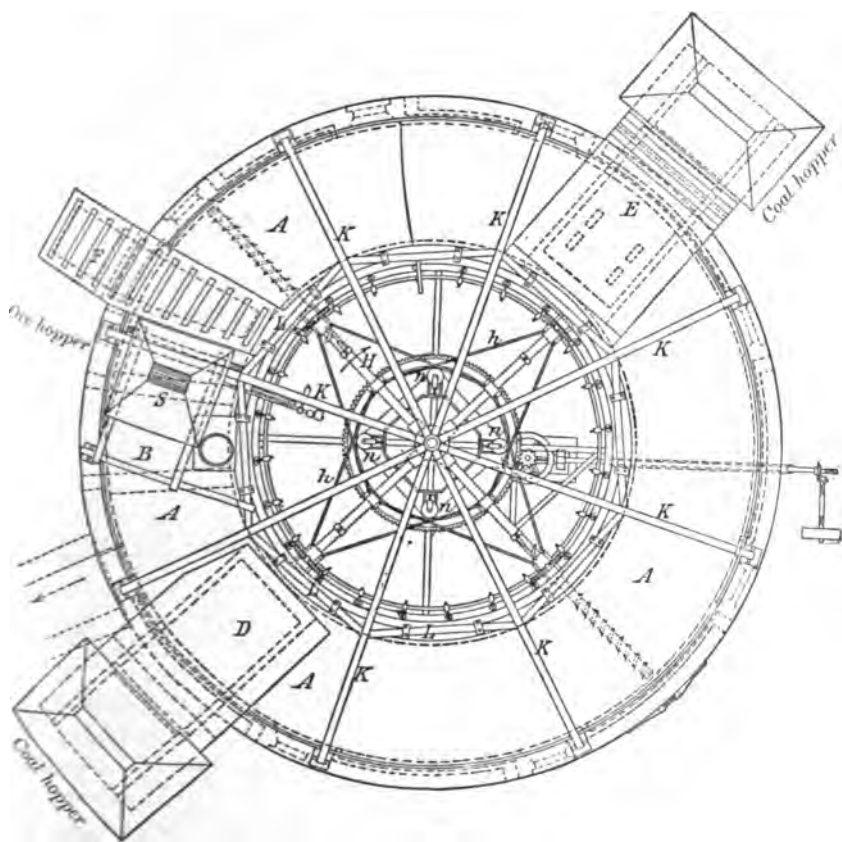


FIG. 20.

blades, and is at the same time itself heated and assists in effecting the oxidation of the ore. A certain amount of air is also introduced in a heated state by traversing passages in the outer wall. No air is needed in the first part of the hearth in which the ore is heated up; the blast is, therefore, cut off opposite the ore hopper by means of valves (Figs. 20, 21).

The ore is fed into the hearth automatically from the hopper *S* (Fig. 21), and distributed by the stops *c* on rabble-arms. It is gradually moved forward by the rabbles and discharged at *B* into a car. The inner wall of the furnace is strutted with iron rails. The slot in the wall is closed by a steel strip 1 foot high (Figs. 26 and 27), which moves with the rabble-arms, and is pressed against the edges of the slot by weighted bell-crank levers; these levers are pivoted upon a ring of angle-iron, bolted to the rabble-arms. The fireplaces have step-grates (Figs. 24 and 25); the fuel (coal) is fed by means of hoppers with automatic feed mechanism.

There are 4 rabble-arms, and the machinery for working these and the blast consumes 2 horse-power. One man attends the furnace in a 12 hours shift.

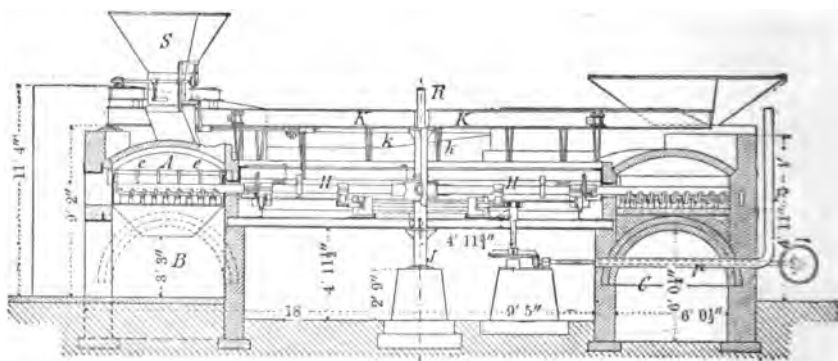


FIG. 21.

The *Brown horseshoe furnace* is a circular furnace with a considerable gap, thus taking the form of a horseshoe.

Its construction, as built by Messrs. Fraser and Chalmers, of Chicago, is shown in Figs. 29 to 35. Fig. 29 is a ground plan; Fig. 30 a vertical section through the furnace proper; Fig. 31 a vertical section through the hearth and flue; Fig. 32 a vertical section through the flue to the stack; Fig. 33 a vertical section through the fire-grate and hearth; Fig. 34 a vertical section through the rear end of the furnace, where the ore is discharged; and Fig. 35 a vertical section through the front or charging end.

As is shown by the plan of the furnace, the hearth occupies about four-fifths of the annular space, one-fifth of the latter lying between the two ends of the hearth; this latter space is left free and serves to cool the rabbles passing over it. On either side of the hearth there are annular divisions which are connected with the hearth by a broad

slot. In the division nearer to the centre a rail is laid upon which carriages run connected with the rabbles. In the outer division a path of hard fire-brick tiles is laid, on which run carriages fitted with broad wheels, and also connected with the rabbles. These carriages, and the rabbles attached to them, are kept in motion by a circular endless wire rope running over guide sheaves and tension pulleys.

There are three fireplaces situated outside the outer circumference of the hearth; the flames pass through a short horizontal flue, and thence through an aperture in the arch into the hearth itself

FIG. 22.

FIG. 24.

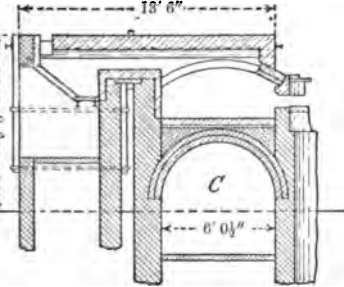
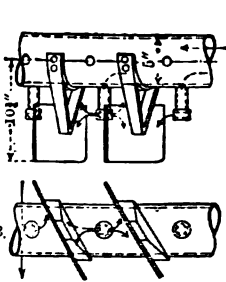


FIG. 26.



FIG. 27.

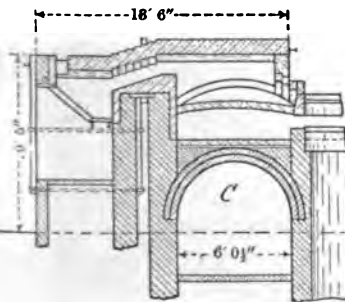


FIG. 25.

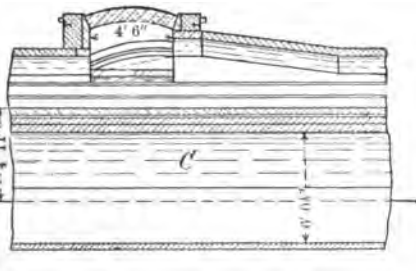


FIG. 28.

(Fig. 33). They there unite and traverse the length of the hearth, escaping through several flues close to the charging end of the furnace; these flues lead into a main flue which communicates with the stack situated at the centre of the circle enclosed by the furnace (Figs. 29 to 32).

The power consumption of the furnace is said to be  $1\frac{1}{2}$  horse-power.

The ore is fed in automatically at the flue end of the furnace (Figs. 35 and 29) and carried forward by the rabbles, of which there

are two, to the other end, where it is discharged. The furnace is closed at either end by two pairs of doors of sheet-iron hung on hinges, which are lifted by the motion of the rabblers and then close automatically. These doors are a short distance apart (Fig. 34), and are so arranged that one closes before the other can open, so that the

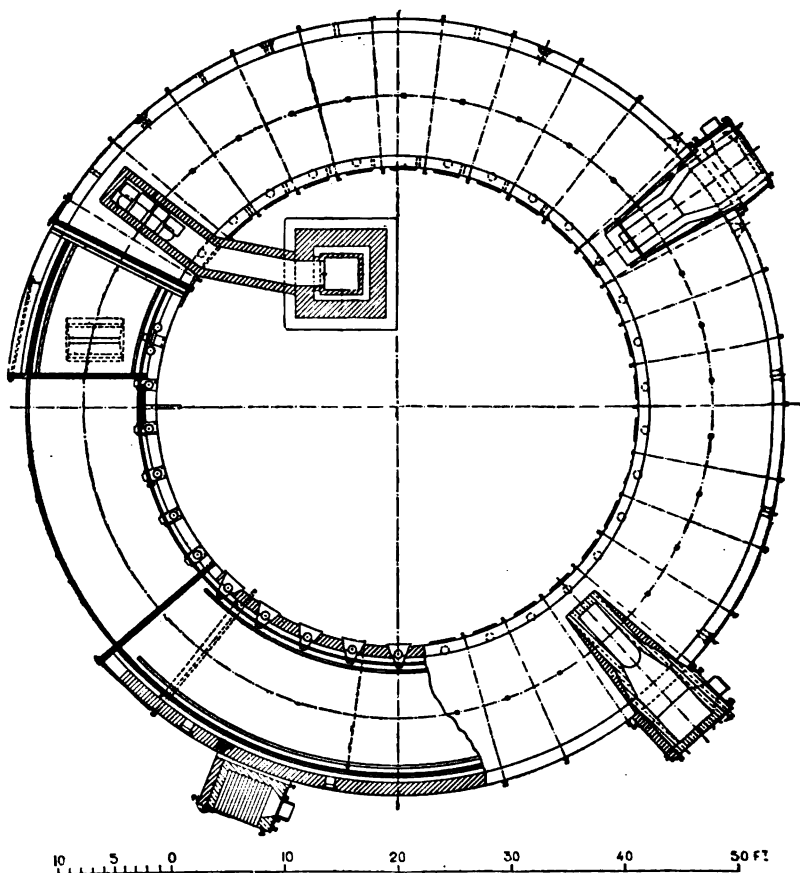


FIG. 29.

admission of cold air at the extremities of the furnace is prevented. At intervals in the outer walls of the furnace are peep-holes which serve also as air inlets.

This furnace is used with success at the Glendale Zinc Works South St. Louis and at Collinsville, for the roasting of blende.

At the works of the Collinsville Zinc Co., Collinsville, Illinois.

such a furnace with four fire-places calcines in 24 hours 10 tons of blende with 30 per cent. of sulphur down to 0·85—1 per cent. of sulphur, with a fuel consumption equal to 6 tons of refuse slack; on account of the inferior quality of the coal, the above figure is no criterion of the real consumption.

The construction of an elliptical Horseshoe furnace is shown in Figs. 36 to 39. The hearth is 180 feet long, and 8 feet wide. The fire-places are built along the inner circumference of the furnace.

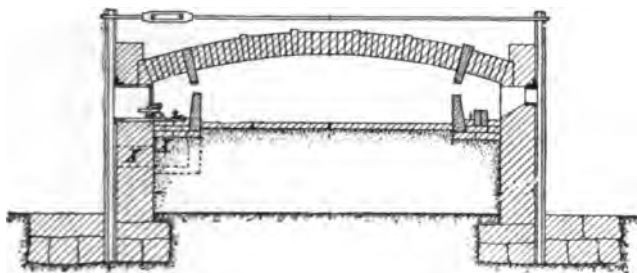


FIG. 30.

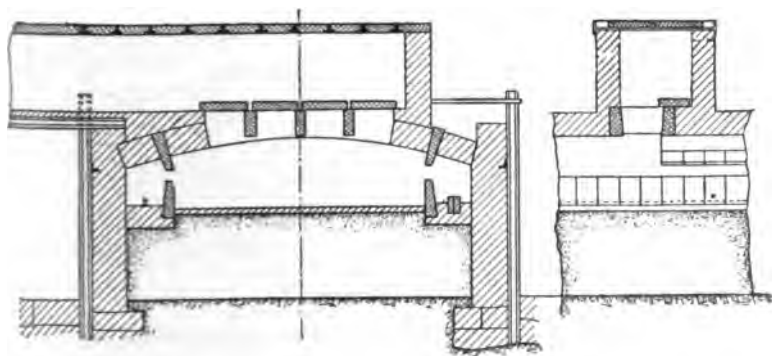


FIG. 31.

FIG. 32.

The author has no information as to the application of this furnace for the roasting of blende.

A long furnace similar to Ropp's (Vol. I. p. 88), adapted for firing with natural gas, has been devised by J. P. Cappeau,<sup>1</sup> and introduced into Jola.<sup>2</sup> This is a modification of the Ropp furnace. Among others may be mentioned Hall's<sup>3</sup> furnace, a modification of Wethey's; and the Zellweger<sup>4</sup> furnace, which is fired with natural gas.

<sup>1</sup> U.S. Pat. No. 691112, Jan. 14, 1902.

<sup>2</sup> *The Mineral Industry*, p. 666, 1902.

<sup>3</sup> U.S. Pat. No. 677510, July 2, 1901.

<sup>4</sup> Ingalls, *The Metallurgy of Zinc and Cadmium*, p. 112.

*Calcination in Reverberatory Furnaces with Movable Hearths*

Reverberatory furnaces with movable hearths have only been used exceptionally on account of their high consumption of fuel and their comparatively small output compared with that of fixed furnaces; and on account of these objections, as also on account of the high temperature required for calcining blende, they are not likely to come into extensive use. Up to the present, they have only been employed

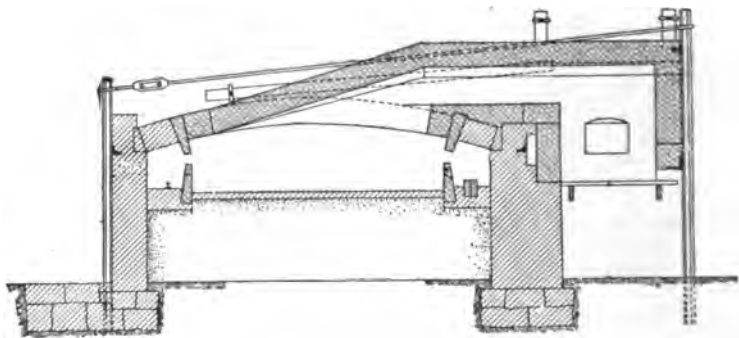


FIG. 33.

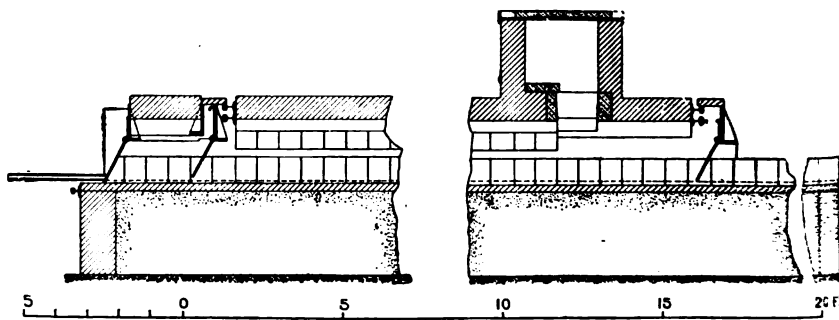


FIG. 34.

FIG. 35.

with advantage for the chloridising roasting of copper ores, for which process a very low temperature is required (see Gibbs and Gelstharpe furnace, Vol. I., page 102), as also for the calcination of tin ores containing arsenical pyrites, which likewise does not require a high temperature (Brunton furnace, see under Tin), and then only in districts where the cost of labour is high.

Kuschel and Hinterhuber have designed a furnace for roasting blende, which has been used at Johannisthal in Lower Carinthia<sup>1</sup>

<sup>1</sup> *Berg- und Hüttenm. Ztg.* 1871, p. 321; 1872, p. 200.

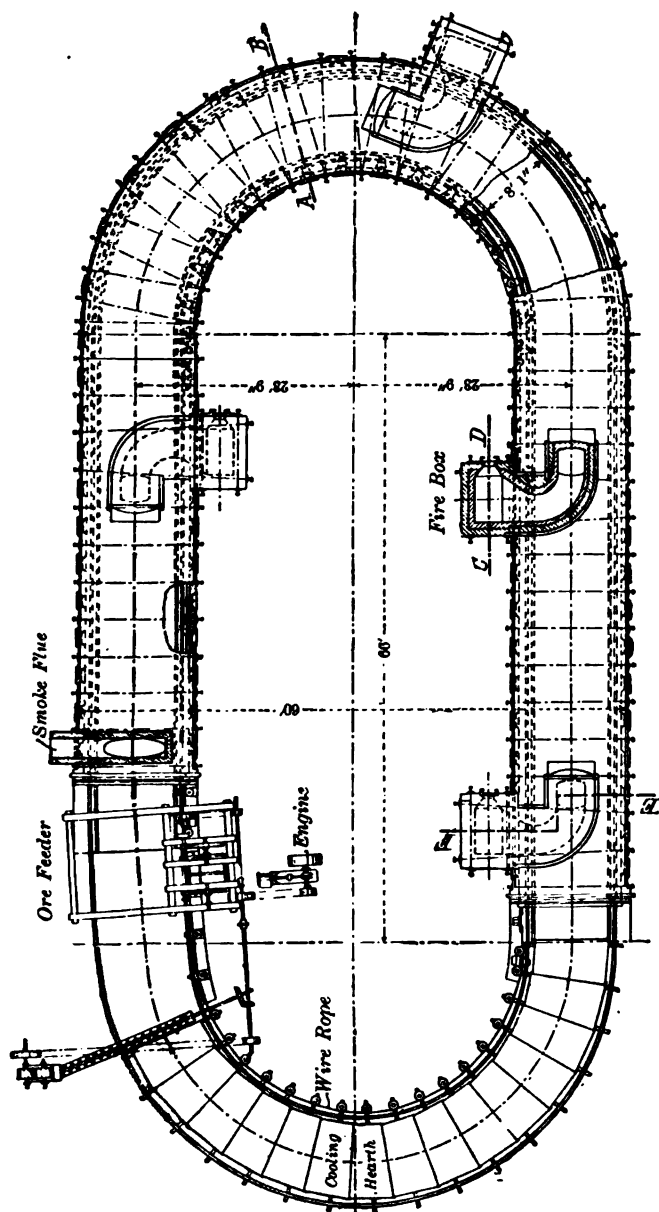


FIG. 86.

This furnace is provided with a round hearth capable of revolving, and with rabble-teeth of fire-brick, which pass through the roof of the furnace, and can be withdrawn from the rabble-arm, but are fixed

during the progress of the calcination. There are two rabble-arms, each with five teeth. These teeth are so arranged that as the hearth revolves, those in one arm occupy the position of the furrows produced by those in the other arm. These teeth are hollow, and serve also for the introduction of the powdered ore into the furnace. When the oven is to be charged, the upper ends of the teeth are opened, these being closed during the progress of the operation by clay plugs. They are raised, and by means of a funnel powdered ore is introduced into them. By the slow turning of the hearth the ore then becomes distributed over it. When the furnace is to be emptied, a grating

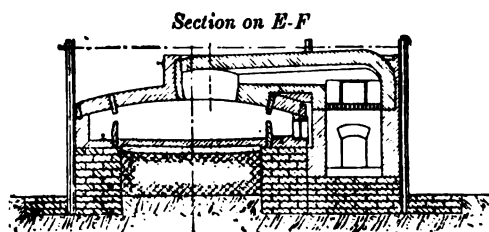


FIG. 37.

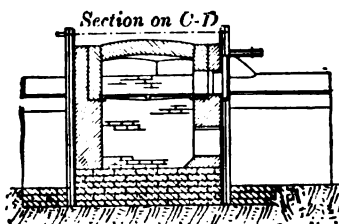


FIG. 38.

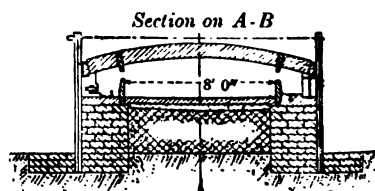


FIG. 39.

formed of inclined iron plates, which is withdrawn into a radial slot in the furnace arch when not in use, is let down upon the hearth, as in the case of the Gibbs and Gelstharpe furnace, and by this means the calcined ore is pushed into four apertures at the edge of the hearth, and thence into a vault beneath the furnace. The diameter of the hearth is 13 feet, the height at the centre is 20 inches, and at the circumference 7 inches; the arch is 12 inches in thickness. The furnace is fired by means of two grates lying side by side, the products of combustion escaping through 13 flues opposite to the fireplace. In order to promote calcination, water vapour is injected in the last stages. In 24 hours 1 to 2 tons of blende are said to be roasted in this furnace, with a consumption of 1.2 tons of coals. The roasting



is said not to be so complete as might be desired. On account of the above-named objections, this furnace has not come into general use.

In the same category may be placed the furnaces of Argall,<sup>1</sup> Blake<sup>2</sup> and Godfrey.<sup>3</sup>

### *Calcination in Reverberatory Furnaces with Movable Working Chambers*

These furnaces are composed of rotating cylinders working intermittently or continuously, and have up to the present been used with great advantage for the oxidising roasting of copper ores and for the chloridising roasting of silver ores, in districts where wages are high. So far as is known to the author, they have not been used for calcining zinc blende, though there is no doubt that zinc blende could be calcined in such furnaces. Considering the long time which the complete calcination of blende requires, and the high temperature requisite in the last stage, continuous-acting furnaces (inclined cast or wrought-iron cylinders, with fire-proof lining and automatic feed arrangements) should be more satisfactory than those that work intermittently (*e.g.*, Brückner furnaces). As it is doubtful whether calcination could be completed in one of these cylinders, it might, in case of necessity, be requisite to combine several of these furnaces, one after the other. Their use would only be justified in districts where wages are very high.

### THE NEUTRALISATION OF THE ACIDS OF SULPHUR EVOLVED BY CALCINATION IN REVERBERATORY FURNACES

When zinc blende is roasted in reverberatory furnaces, whether it has undergone a previous preliminary roasting or not, the neutralisation of the products of calcination, containing sulphur dioxide, together with a small quantity of sulphur trioxide, plays a very important part; it is only in countries which are as yet sparsely cultivated, and in districts in which vegetation has already been destroyed by the effect of these gases, that the latter may be discharged direct into the atmosphere in their concentrated form; in all other places they must be neutralised. For example, in Prussia, the main seat of the production of zinc, such gases may only be allowed to

<sup>1</sup> U.S. Pat. No. 653202, July 10, 1900.

<sup>2</sup> Ingalls, *The Metallurgy of Zinc and Cadmium*, p. 116.

<sup>3</sup> U.S. Pat. No. 637864.

escape into the air when their contents of sulphur dioxide are so small that no injurious action upon the vegetation is to be feared. The best and most profitable method of neutralisation of these gases, viz., the conversion of sulphur dioxide into sulphuric acid, cannot be applied to the gases evolved from reverberatory furnaces, because the sulphur dioxide escapes from it in a condition of such excessive dilution (less than 2 per cent. by volume), and because it is intermixed with the products of combustion of ordinary fuel, which have an injurious effect upon the nitrous gases in the manufacture of sulphuric acid. For this reason reverberatory furnaces are especially used for calcining blende in those cases in which the utilisation of sulphur dioxide for the manufacture of sulphuric acid is impossible, owing to the absence of any market for the latter. The processes, by which the products of combustion containing sulphur dioxide can be neutralised, admit only exceptionally of the latter being utilised at the same time. As a rule, these operations increase markedly the cost of calcination. All attempts up to the present not only to neutralise but at the same time to utilise the gases from reverberatory furnaces have remained fruitless, because they have been found to be too costly; there is here, therefore, a wide field open to metallurgical discovery. Sulphur dioxide has been rendered innocuous by diluting the gases containing it with air, or by absorbing it by means of water, of sulphuric acid of 50° B., of milk of lime, of limestone and water, of oxide of zinc, of basic zinc carbonate, of magnesia, of ferric oxide, of ferric sulphate, of solution of sodium sulphide, of calcium sulphide, or of iron kept moist, and by conveying it into waste heaps of alum ores.

The dilution of sulphur dioxide by means of air can be performed by allowing the products of calcination to escape from the furnaces into the upper regions of the atmosphere by means of high stacks. The sulphur dioxide thus produced diffuses through extensive layers of air, and is diluted by these to such an extent that, on its descent, it no longer has an injurious effect upon vegetation. This dilution of sulphur dioxide can only, however, be attained when the quantities of blende to be roasted are limited, and when, therefore, only inconsiderable amounts of gases are evolved, as otherwise the injurious effect of these gases becomes noticeable in time in a wide area surrounding the calcining works. If the contour of the country admits of it, such stacks should be situated on the tops of high hills and connected with the furnaces by means of inclined flues. The height of these stacks varies with their position between 330 and 500 feet (at Hamborn 333 feet, at Freiberg 466 feet). As the draught

of a stack cannot be improved by increasing its height above 160 feet, all prime costs which are necessitated by the construction of a stack higher than this must be charged to the neutralisation of the sulphur dioxide.

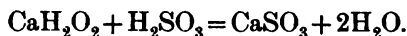
These first costs are very considerable, but only result in a small working charge, because the actual neutralisation of the sulphur dioxide then costs nothing. If, therefore, comparatively small quantities of these gases have to be liberated, the best method of rendering them innocuous is by means of such high stacks.

The products of calcination can only be imperfectly neutralised by the help of water, because water either falling in the form of rain or trickling through a coke tower absorbs only comparatively little sulphur dioxide from diluted gases, and scarcely any from hot gases. The experiments which have been tried to remove sulphur dioxide from the gases given off from a reverberatory furnace by means of lead towers filled with coke, over which water trickles, were not only unfavourable as regards the absorption of the sulphur dioxide, but also required towers of large area, together with powerful fans, in order to maintain the draught, as well as suitable dust chambers, and the previous cooling of the gases. The method of absorbing the sulphur dioxide by means of water has, therefore, not come into use. The absorption of sulphur dioxide from the products of combustion by means of sulphuric acid at 50° B., which was attempted with the blende calcining furnaces of the chemical factory at Rhenania, near Stolberg, has also been found imperfect, because the sulphuric acid, whilst it readily absorbed the sulphur trioxide contained in small quantity in these gases, did not absorb the sulphur dioxide. The plant employed was a tower filled with coke over which the sulphuric acid was allowed to trickle. Apart from the imperfect absorption of the sulphur dioxide, the same objections arose as in the case of absorption by water. This method, therefore, has found no further application.

Sulphur dioxide and sulphur trioxide are readily absorbed by milk of lime, calcium sulphite and sulphate being produced. The former is gradually converted on contact with air into the latter salt. The product of the absorption is, therefore, a mixture of calcium sulphite and sulphate, which, as experiments at the Hohenlohe Works, near Kattowitz, in Upper Silesia, have shown, may be used either as a disinfectant, as a vermin destroyer, or as manure when mixed in certain proportions with animal manure, or in the case of well-manured ground rich in humus, even without such admixture. The quantities of this salt for which a market can be found are, however,

so small compared with the great quantities in which it is produced that it is not only worthless, but may even be looked upon as a waste product occupying much space, and, therefore, troublesome.

The absorption of the sulphur dioxide takes place in accordance with the following equation:—



It takes place on contact and requires an excess of the absorbing solution in order to be complete. The absorption is, therefore, carried out by exposing the gases in towers to a rain of milk of lime, and again using the product thus obtained, which still contains a considerable quantity of free calcium hydrate, as an absorbent. The composition of the salt is as follows, according to Dr. Grosser of Kattowitz:—

CaO . . . . .	37·75
MgO . . . . .	1·45
Al <sub>2</sub> O <sub>3</sub> . . . . .	4·14
Fe <sub>2</sub> O <sub>3</sub> . . . . .	1·10
SO <sub>2</sub> . . . . .	38·40
SO <sub>3</sub> . . . . .	2·85
CO <sub>2</sub> . . . . .	4·15
Soluble SiO <sub>2</sub> } . . . . .	5·53
and residue }	
H <sub>2</sub> O . . . . .	3·40
	<hr/>
	98·77

According to this analysis, the quantity of calcium sulphite amounts to 72 per cent., and of calcium sulphate to 4·84 per cent. Upon the average the salt, as produced at the Hohenlohe Works, contains about 34 per cent. of SO<sub>2</sub> and 5 per cent. of SO<sub>3</sub>, equivalent to 64 per cent. of calcium sulphite and 8·5 per cent. of calcium sulphate, together with 6 to 10 per cent. of water.<sup>1</sup> The absorption of sulphur dioxide by milk of lime is made use of in several of the large works in Upper Silesia, but is carried out on the largest scale at the above-mentioned Hohenlohe Works. At these works the products of combustion are drawn by means of stacks upwards and downwards through towers down which milk of lime is trickling, and they escape, containing only very small quantities of sulphur dioxide, into a stack 328 feet high, by which the last remaining portions of sulphur dioxide are carried into such a high stratum of the atmosphere that they no longer

<sup>1</sup> Kosmann, *Oberschlesien*, &c., p. 199.

exert any injurious action. The solution trickling down the towers is led into sumps in which the salt is deposited. It is lifted out from these mechanically and piled in heaps, whilst the clear solution is used again for dissolving fresh portions of gas. Although the process is expensive, yet it completely fulfils its purpose, and has up to the present not been replaced by any other method.

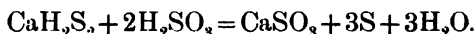
The sulphur dioxide of the gases escaping from reverberatory furnaces can also be neutralised by means of water and limestone or dolomite. For this purpose towers are filled with fragments of the above-mentioned substances and water is allowed to trickle through them. The sulphur dioxide in the gases passing up these towers forms calcium or magnesium sulphite. The absorption in this method is less energetic than it is by milk of lime, and requires towers of large area, considerable quantities of fluid, and a good draught. It has, therefore, not yet come into use at zinc works.

Zinc oxide, basic zinc sulphate and magnesia have only been used experimentally for neutralising the sulphur dioxide from blende calcining furnaces. These bodies form sulphites of zinc or magnesium, which are readily decomposed on heating, with the evolution of concentrated sulphur dioxide. By their use, therefore, the diluted sulphur dioxide of the gases escaping from the furnaces can be concentrated, whilst the absorbent is regenerated. These sulphites by long exposure to the air and moisture can also be converted into sulphates. As, however, before sulphur dioxide could be absorbed the gases had previously to be cooled down, and as flue-dust had also to be removed from them; as, moreover, during their absorption a considerable quantity of sulphates was formed, together with sulphites, which former salts are only imperfectly decomposed when the mixture is heated for the production of concentrated sulphur dioxide, the neutralisation of furnace gases by means of the substances in question has not come into extended use. Experiments to convert the dilute sulphur dioxide of the furnace gases into concentrated sulphur dioxide by means of water have failed on account of the low absorbing power of water upon dilute sulphur dioxide. The object of the experiments was to absorb sulphur dioxide by means of water and then to evolve it in a concentrated form by heating the solution. This process, which will be explained more fully further on, is only available when the gases contain at least 4 per cent. by volume of sulphur dioxide.

Moist ferric oxide absorbs sulphur dioxide slowly with the formation of ferrous and ferric sulphates. Ferric sulphate absorbs it with the formation of ferrous sulphate. On account of the slow rate of

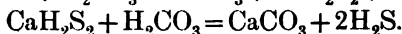
absorption and the low value of the products, neither of these methods has come into use. All attempts to produce sulphur by the reduction of the furnace gases by the aid of carbon have given most unsatisfactory results. Still less satisfactory were the experiments to separate sulphur by the action of sulphuretted hydrogen upon the dilute gases. A solution of sodium sulphide absorbs sulphur dioxide well, with the formation of sodium sulphate and sulphur, but this process has been found to be too expensive in practice. Solutions of polysulphides of calcium absorb the sulphur dioxide of furnace gases readily with the production of sulphur, but come too expensive. Calcium monosulphide cannot be used as an absorbent on account of its slight solubility in water.

Kosmann<sup>1</sup> has proposed to convert calcium monosulphide into calcium sulph-hydrate, by treating it with carbon dioxide and water, as is done by Chance in his process for treating the residues from the manufacture of soda by the Leblanc process, for the production of sulphuretted hydrogen or sulphur, and to use this calcium sulph-hydrate as an absorbent for the sulphur dioxide of the furnace gases. The oxides of sulphur are absorbed by calcium sulph-hydrate with the formation of calcium sulphite and sulphate, sulphur separating out as is shown by the following equation :—

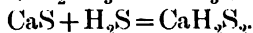
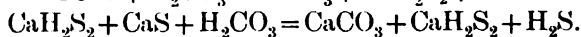
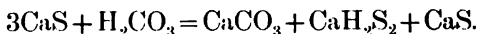


A precipitate of calcium sulphite and sulphate and of sulphur is thus obtained.

By the action of carbon dioxide upon calcium sulphite, calcium sulph-hydrate and calcium carbonate are first formed. On further action the calcium sulph-hydrate is decomposed with the evolution of sulphuretted hydrogen, calcium carbonate being produced :—

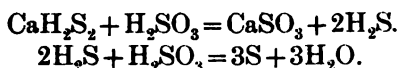


Kosmann interrupts the process when the greater part of the calcium sulphide has been converted into sulph-hydrate, and conducts the sulphuretted hydrogen produced into a further quantity of monosulphide, which is also converted into sulph-hydrate by the sulphuretted hydrogen. According to Kosmann the equations are as follows :—



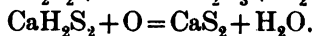
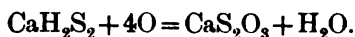
<sup>1</sup> Glückauf, *Berg- und Hüttenm. Ztg.* in Essen, No. 35, May 2, 1904.

Thus four molecules of calcium sulphide and two of carbon dioxide produce two molecules of calcium sulph-hydrate and two of carbonate, or two molecules of calcium sulphide yield one molecule of calcium sulph-hydrate. The solution of calcium sulph-hydrate is blown by means of an injector into the furnace gases, together with water vapour. The sulphur dioxide is then absorbed, as is shown by the following equations:—



Each molecule of sulph-hydrate, therefore, absorbs two molecules of sulphur dioxide with the formation of one molecule of calcium sulphite or sulphate and the production of three atoms of sulphur. As two molecules of calcium sulphide are required for the formation of one molecule of sulph-hydrate if the process were conducted exactly in accordance with the theory, each molecule of calcium sulphide would neutralise one molecule of sulphur dioxide, and at the same time separate  $1\frac{1}{2}$  atoms of sulphur. The sulphur is obtained mixed with calcium sulphite or sulphate. It is removed from this mixture by boiling with caustic lime, whereby calcium polysulphide is produced, the latter being employed as an absorbent for the sulphur dioxide. The greater portion of the sulphur is thereby precipitated with the simultaneous formation of calcium sulphite and sulphate. From the precipitate so obtained the sulphur may be recovered by distillation. The process, though theoretically sound, has not yet come into practical use. Although calcium sulph-hydrate and calcium polysulphide absorb sulphur dioxide far better than does milk of lime, it must, nevertheless, be borne in mind that the production of the carbon dioxide required for the process by the burning of limestone or the combustion of coke entails no inconsiderable cost; that the calcium carbonate produced when the sulph-hydrate is formed cannot be utilised, and thus constitutes a troublesome substance occupying a great deal of space; that the preparation of calcium sulphide by the reduction of calcium sulphate, whenever this cannot be obtained in the form of residues from the Leblanc process, also entails expense; and that of the calcium contained in it, only half can be converted into sulphate or sulphite, whilst the other half is converted into carbonate. From the sulphate or sulphite calcium sulphide can be regenerated, but not from the carbonate. For the production of the requisite calcium sulphide it is, therefore, necessary to add calcium sulphate to the extent of one-half of that entering into the process. Finally, considerably more sulph-hydrate is required

than theoretical calculation would indicate, because the furnace gases always contain oxygen and carbon dioxide, both of which act upon the sulph-hydrate, the former converting the sulph-hydrate partly into calcium hyposulphite and partly into calcium polysulphide in accordance with the equations :—



Whilst calcium polysulphide absorbs sulphur dioxide, the hyposulphite is not affected by it. All the sulph-hydrate which is converted into that salt is, therefore, lost to the process. The calcium polysulphide produced is at the same time less effective as an absorbent than is the sulph-hydrate, seeing that two molecules of the former only absorb three molecules of sulphur dioxide, instead of four molecules, as in the latter case. Carbon dioxide attacks the sulph-hydrate with the formation of sulphur and calcium carbonate, so that this calcium takes no part in the absorption of sulphur dioxide.

Metallic iron moistened with water, as proposed by Winkler, acts well in the case of gases rich in sulphur dioxide, as, for example, those generated in the parting of gold by sulphuric acid, but it is less effective in the case of dilute gases, such as are thus evolved from the blende calcining furnaces. At Flône, in Belgium, the furnace gases have been passed into waste heaps of alum ores by which the latter were rendered soluble. The employment of this process is, however, only possible under very exceptional local conditions. Further information respecting experiments upon the neutralisation of sulphur dioxide will be found in the works of Reich, Freiberg, 1858; Winkler, *Freiberger Jahrbuch*, 1880, p. 50; Schnabel, *Preuss. Zeitschr. f. Berg.-Hütt. u. Salinen-Wesen*, 1881, 29, p. 395; Hasenclever, *Fischer's Jahresberichte*, 1881, p. 173, 1886, p. 257; *Zeitsch. d. Ver. Deutsch. Ing.* 1886; C. A. Herring, *Die Verdichtung des Hüttenrauchs*, Stuttgart, 1888.

#### *Calcination in Combined Reverberatory and Muffle Furnaces*

These furnaces are only employed when a portion merely of the sulphur dioxide evolved on calcining blende is to be utilised in sulphuric acid manufacture, whilst the remainder is to be allowed to escape unused. In this case the sulphur dioxide developed in the muffle furnace is conveyed into lead chambers, whilst that escaping from the reverberatory furnace is either led direct into the air or previously neutralised. The principle of these furnaces is, that the muffles in which the first stage of the calcination of the blende is conducted



shall be heated by the gases of the reverberatory furnace, in which the blende is roasted dead. The muffles may either lie partly inclined or else horizontally. The Hasenclever-Helbig furnace, designed in the year 1874 by Hasenclever and Helbig, and used with great advantage

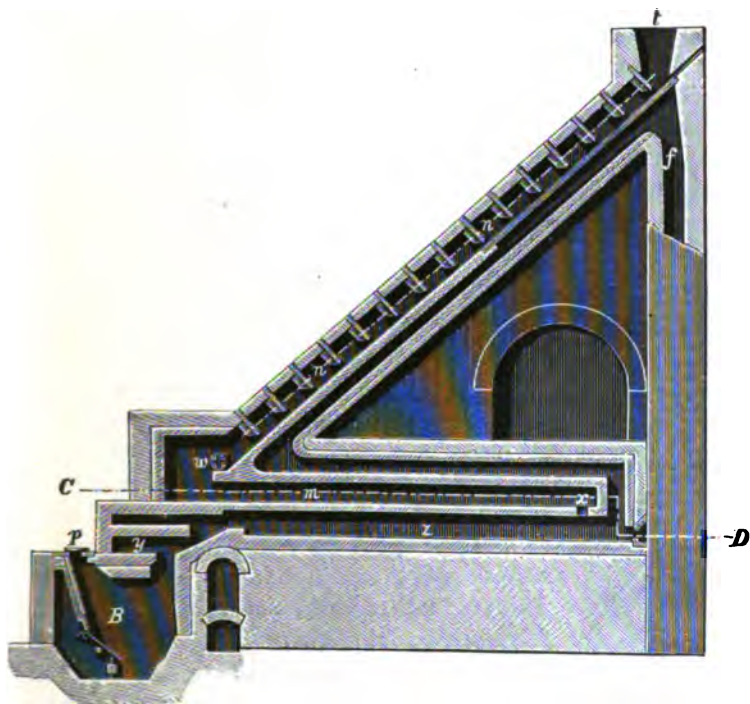


FIG. 40.

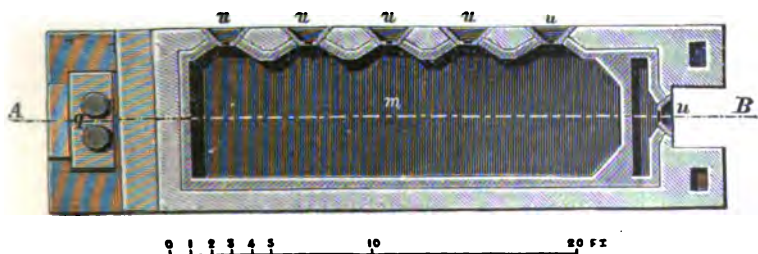


FIG. 41.

in the Rhine districts, Westphalia and Silesia, is a furnace with partly inclined muffle. At present it has been replaced at most works by the muffle furnace to be described further on, which admits of the complete utilisation of the sulphurous gases evolved in calcination. The furnace consists, as shown in Figs. 40 and 41, of a

muffle constructed in two parts, situated over a reverberatory furnace: the lower part of the muffle *m* is horizontal, whilst the upper part *n*, which adjoins it, lies at an angle of  $43^\circ$ . In the inclined portion walls of hard-burnt bricks are built some 20 inches apart, at right angles to the long axis of the muffle, and hang down so far that between their bottom edge and the floor of the muffle there is only a space of less than an inch. The object of these walls is to spread the ore, which is charged at the upper end of the muffle, in a thin bed upon the floor of the latter. In order to enable the products of combustion to pass unhindered by these partition walls, there are lateral openings in them, so that the gas escapes following a sinuous line alternately at one side or the other of the walls, as shown in Fig. 42.

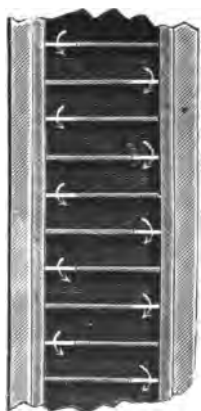


FIG. 42.

The pulverulent blende charged from the hopper *t* at the upper end of the muffle slides along the bottom of the latter, and at definite intervals of time—from 2 to 5 minutes—is carried by the roll *w*, which is driven by a small water wheel, into the lower horizontal portion of the muffle, where it is spread out and further roasted. At the far end of the horizontal portion of the muffle there is an opening *x*, through which the blende is dropped into the working chamber *z* of the reverberatory furnace, where it is roasted dead. The products of combustion of the reverberatory furnace first heat the floor and then the arch of the horizontal portion of the muffle, and then rise up underneath the inclined portion of the latter into the flue *f*. The sulphurous gases evolved in the

horizontal portion of the muffle pass into the inclined portion, where they unite with the gases evolved there, and together escape from the upper end of the muffle into a flue which conducts them to the sulphuric acid chambers. At the end of the muffle the blende will have lost 60 per cent. of its sulphur, still containing from 8 to 10 per cent., whilst the gases that escape from the muffle carry at least 6 per cent. by volume of sulphur dioxide, and are very suitable for sulphuric acid manufacture. The blende is then calcined down to 1 per cent. of sulphur upon the hearth of the reverberatory furnace, which forms a long-bedded calciner with working doors along one of its longer sides. The furnace may be fired either by a grate or by gas. In the figure it is shown as fired by gas, a Boëtius producer, *B*, being employed. The air, which is heated in the walls of the latter, enters at *y*; the fuel is charged at *p*. The temperature in the

inclined portion of the muffle is as high as the melting point of antimony ( $432^{\circ}$  C.). In this furnace 3 to 4 tons of zinc blende can be calcined down to 1 per cent. of sulphur in 24 hours, with a consumption of coal equal to 28 to 50 per cent. of the weight of the raw ore. At the Recke Works such a furnace was formerly in use calcining  $3\frac{1}{2}$  tons of blende down to 1 per cent. of sulphur in 24 hours, with a consumption of 2 tons of coal.<sup>1</sup>

At Oberhausen<sup>2</sup> the furnace had the following main dimensions: Cross section of the gas producer, 2 feet by 6 feet; floor of the horizontal portion of the muffle, 6 feet by 24 feet 7 inches; of the inclined portion of the muffle, 6 feet by 32 feet 10 inches; of the reverberatory furnace, 6 feet by 18 feet 8 inches. Of the sulphur contents of the blende 50 per cent. was utilised by means of the muffle. At the commencement of calcination, it contained 26.44 per cent. of sulphur; on leaving the inclined portion of the muffle, where there was a low red heat, 8.20 per cent.; on leaving the horizontal portion of the muffle, where there was a bright red heat, 6.20 per cent.; at the end of the calcination 0.55 to 1.30 per cent. In 24 hours,  $3\frac{1}{2}$  tons of ore were roasted, with a consumption of 21 cwt. of coals. Five workmen on a shift worked the calciner. The gases escaping from the muffles into the sulphuric acid chambers carried from 5 to 6 per cent. by volume of sulphur dioxide. This furnace has, as compared with reverberatory furnaces, the drawback of heavier first cost and requires a heavier outlay for wages, but has, on the other hand, the advantage of utilising half the sulphur dioxide evolved during calcination. But even allowing for the latter advantage, the costs of calcination in this furnace are heavier than the costs of calcination in long-bedded calciners. As compared with the muffle furnaces, on the other hand, it has the objection that only a portion of sulphur dioxide evolved can be utilised. It has therefore been replaced by muffle furnaces.

A combined reverberatory and muffle furnace with horizontal muffles, which gives very good results, is used at the Recke Works in Upper Silesia. It consists of a reverberatory furnace, over which there are two horizontal muffles connected together. The flame passes first over the hearth of the reverberatory furnace, surrounds first the lower and then the upper muffle. The products of combustion, together with the sulphur dioxide evolved from the reverberatory furnace, pass into towers in which they are freed from any sulphur

<sup>1</sup> *Berg- und Hüttenm. Ztg.* 1877, p. 71.

<sup>2</sup> *Mahler, Annalen des Mines*, vol. vii., book iii., p. 152, 1885.

dioxide and trioxide that they contain, and then into the stack. The sulphurous gases evolved in the lower muffle pass into the upper muffle, and thence, together with the gases evolved in the latter, into the sulphuric acid factory. The blende is charged at the end of the upper muffle, passes, after it has traversed this, into the lower muffle, and finally into the reverberatory furnace. In this furnace 6 tons of blende are calcined down to less than 1 per cent. of sulphur in 24 hours, with a consumption of coal equal to 30 per cent. of the weight of the raw ore. This furnace, which is a modification of the Hasenclever furnace, gives better results than the original.

### *Calcination in Muffle Furnaces*

The necessity of neutralising the sulphurous gases evolved in calcining blende, and the difficulty of doing this when blende is calcined in reverberatory furnaces, have promoted the introduction within the last 20 years of muffle furnaces, in which the production of gases rich in sulphur dioxide, that is, containing 5 to 8 per cent. by volume and therefore suitable for sulphuric acid manufacture, can be combined with a complete calcination of blende. These furnaces depend upon the principles that the calcination must be conducted by heating the muffles externally by burning fuel, as also internally by the help of the heat developed by the oxidation of the sulphide of zinc; that the muffles should be arranged one below the other, and so combined that the blende which is to be roasted passes from above downwards, whilst the gases generated inside them, as well as those heating them from outside, move in the opposite direction. The first furnace designed on these principles, which admitted of the utilisation of the whole of the sulphur dioxide evolved in the calcination of blende for sulphuric acid manufacture, was designed by M. Liebig. He was followed by Grillo, Hasenclever, and a number of other inventors with furnaces depending upon the same principles, but of widely different design. These modern muffle furnaces have given such far better results than the older forms previously used that they have replaced reverberatory furnaces as well as the combined reverberatory and muffle furnaces, wherever it is at all possible to find a market for sulphuric acid or to utilise sulphur dioxide in any other way. The furnaces that are at present in actual operation are built with fixed muffles. The ores are rabbled by means of hand power or mechanically. Muffles in the

form of rotating cylinders have been proposed and patented, but have not yet come into regular use.

We must therefore distinguish :—

Calcination in Fixed Muffle Furnaces with hand rabbling.

Calcination in Fixed Muffle Furnaces with machine rabbling.

Calcination in Rotating Muffle Furnaces.

### *Calcination in Fixed Muffle Furnaces with Hand Rabbling*

The most important furnaces of this class are those of Liebig and Eichhorn, and of Hasenclever. A third furnace of the same type is that of Grillo.

The Liebig and Eichhorn furnace depends upon the principle of conveying the blende through a number of chambers lying

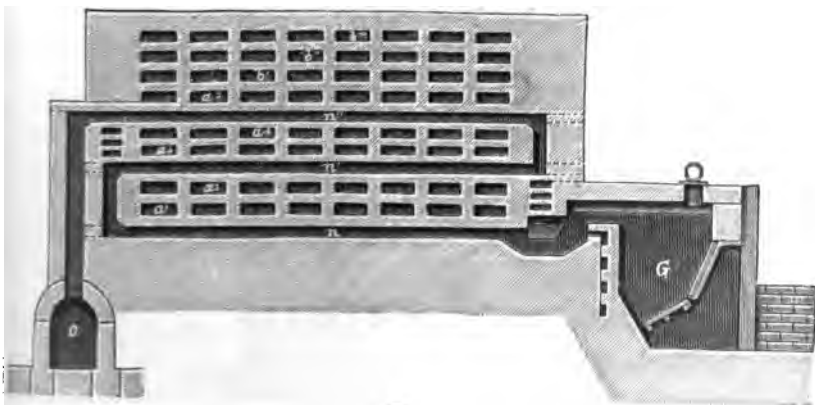


FIG. 43.

one below the other, and of allowing the air required for oxidation to enter the chamber in a heated condition. The three upper chambers are heated by heat evolved by the oxidation of the sulphide of zinc similarly to the shelves of the Maletra furnace, whilst the lower chambers are heated externally by gas firing. The construction of the furnace, as patented,<sup>1</sup> is shown in Figs. 43 and 44. It consists of a shaft provided with muffles  $a^1, a^2, a^3, a^4, a^5, b^1, b^2, b^3$ , which are accessible by the working doors  $c$  disposed alternately along the two shorter sides. The heating of the chambers  $a^1, a^2, a^3$  and  $a^4$  is performed by means of the producer gas generated in the producer  $G$ , this being burnt in a stream of air heated by traversing flues in the walls of the producer. The flame traverses

<sup>1</sup> D. R. Patent, No. 21032.

first the flues  $n, n$ , rises, passes through the flues  $n', n'$ , traverses these flues, again ascends, and finally traverses the flues  $n'', n''$ , from which it escapes into the flue  $o$  leading to the stack. The air required for the oxidation of the sulphide of zinc enters by the opening  $d$ , passes into the flue  $e$ , and from the latter into the muffle  $a^1$ , being warmed on its passage through the walls of the flues  $n, n$ , and then traverses the separate muffles one after the other, oxidising the sulphide of zinc inside them. The zinc blende is delivered by means of a charging hopper  $f$  into the topmost muffle  $b'''$ , and is transferred from the latter after some time into the muffle lying immediately

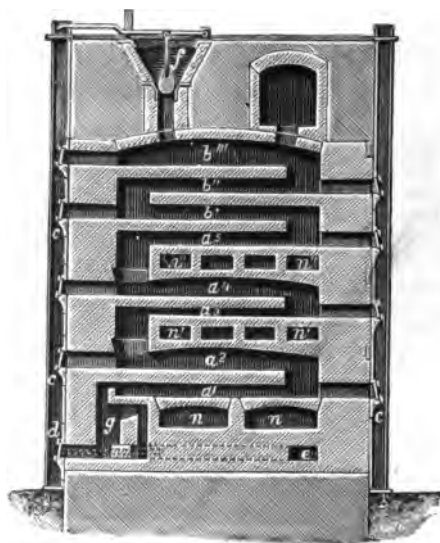


FIG. 44.

beneath it. From this it is removed at definite intervals into the next lower lying muffle, and so it advances until it is drawn out from the bottommost muffle into the chamber  $g$  in a calcined condition. In the three topmost muffles the temperature is maintained entirely by the heat generated by the oxidation of the sulphide of zinc; in the lower chambers but little heat is derived from the blende, and they are therefore heated by means of producer gas from the outside. As this method of firing heats the lowest muffle to the highest temperature, the ore in its descent is exposed to gradually increasing temperatures, and finally reaches the end of the lowest muffle containing only 0.1 per cent. of sulphur. The sulphur gases traverse each muffle from below upwards and finally escape from the topmost

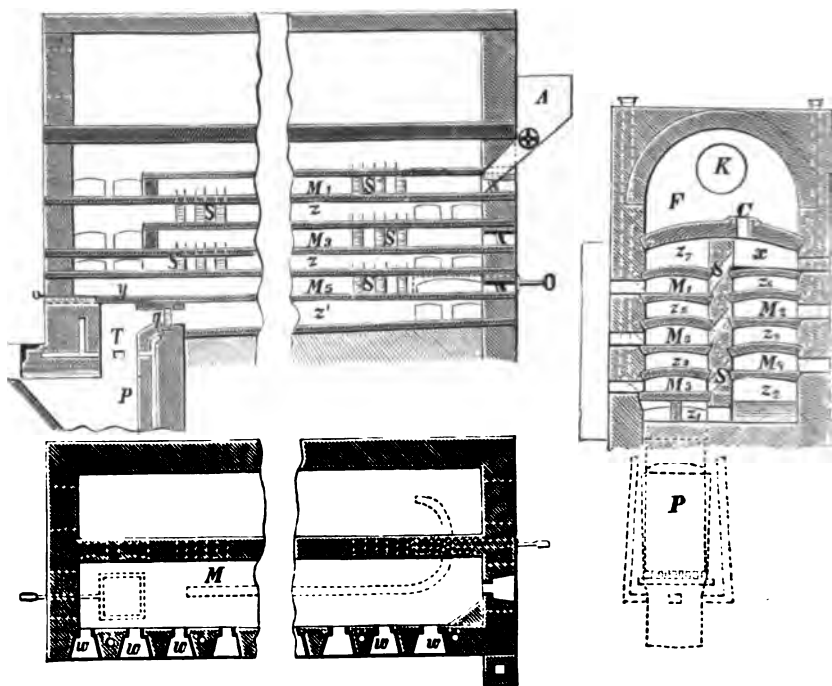
muffle containing 6 to 8 per cent. by volume of sulphur dioxide. The ore remains in each muffle from 6 to 8 hours, and requires 48 hours to traverse the furnace. In experiments made to determine the degree of desulphurisation of the ore in the various muffles, it was found that it contained 27·8 per cent. of sulphur on charging into the topmost muffle; after being there 6 hours, 24·9 per cent.; in the four following muffles, 17·3, 13·2, 2·3 and 0·2 per cent. respectively, and when drawn from the bottom muffle only 0·1 per cent. According to Eichhorn<sup>1</sup> such furnaces yield in 24 hours from 4·2 to 4·5 tons of blende calcined down to 0·1 per cent. of sulphur, with a consumption of 0·8 ton of coal, 2 men being required on a 12-hour shift. Such furnaces are in use at Letmathe and at Hamborn, near Oberhausen. In Hamborn a block consists of 4 furnaces, and yields in 24 hours 5 tons of calcined ore, with a consumption of 20 to 25 per cent. of coal, 2 men on a 12-hour shift working the furnace. The most recent furnaces of this type are those with 3 or 4 long-bedded muffles of which the lowermost is heated from below. In some furnaces there is also a flue between the bottommost muffle and the next higher one, so that the lowest muffle is heated from above and below, the next from below only.

Grillo's furnace is shown in Figs. 45 to 47. It consists of the muffles  $M^1$  to  $M^5$ , and the flues  $Z^1$  to  $Z^7$ . The ore is delivered by means of the hopper  $A$ , provided with a charging roller, into the topmost muffle which it is made to traverse, and at its end drops through the inclined slots  $S$  into the next lower muffle. After passing through this, it is dropped into the muffle below and so gradually reaches the bottommost muffle, at the end of which it is drawn out through a working door. The products of calcination escape through the slots  $S$  out of the lower into the next higher muffle, and after they have travelled through all the muffles from below upwards, escape into the chamber  $x$ , from which they pass through the vertical flue  $C$  into the dust chamber  $F$ , and thence through the flue  $K$  into the sulphuric acid chambers. The furnace is fired by gas, but can also be fired by a grate. The gases generated in the producer  $P$  mix at  $T$  with air which has been warmed by traversing the furnace walls. The flame surrounding the muffles on three sides passes upwards through the flues  $Z^1$  to  $Z^7$ , escaping from the topmost one into the stack;  $w, w$  are the working doors. Each individual muffle is 29 feet 6 inches long. By drawing out the slide  $y$  and closing the flue  $Z^1$ , by means of the damper  $q$ , the muffle furnace can be converted into a reverberatory furnace. This furnace has been found

<sup>1</sup> Fischer's *Jahresber.* 1889, p. 322.

to be less efficient than that of Liebig, and has therefore been replaced at the Hamborn Works, where it was in use, by the Liebig furnace.

The Hasenclever furnace consists of several (three or four) muffles lying one above the other and united by means of vertical flues, and heated by the flames from a fire-grate. The blende to be roasted is admitted by means of a charging hopper into the topmost muffle, and is pushed forward, from time to time, as is done in long-

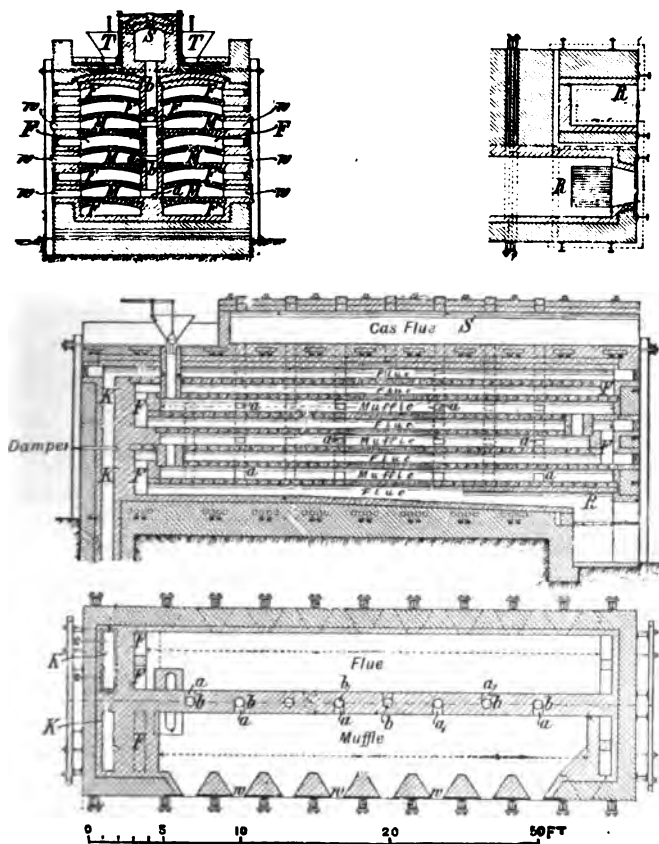


FIGS. 45-47.

bedded calciners; through a vertical flue at the end of this muffle it drops into the second muffle placed below the former, in which it is pushed forward in the same way, drops thence into the third muffle, and so on. At the end of the bottommost muffle the calcined ore is drawn out through a working door. The flame follows the opposite direction to the calcined ore, passing upwards, and on its way heats the floors and arches of the various muffles. The products of calcination either pass from below upwards through all the muffles or else escape from the rear of each muffle by vertical flues, from which the



gas escapes to a main flue leading to the sulphuric acid works. With ores rich in sulphur, two or three muffles have also frequently been placed one above the other, and the flame has been allowed to heat the floor of the lower and the roof of the upper muffle; in order to economise heat, these furnaces are always built in pairs back to back. The construction of the Hasenclever furnace is shown in



FIGS. 48—51.

Figs. 48 to 51, which represent a pair of such furnaces. *R, R* are the grates, *M, M* are the individual muffles, *F, F* are the flues by which the flame passes from below upwards, and from the topmost of which it then escapes from the flue *K* into the stack. *T, T* are the charging hoppers from which the blende to be roasted is conveyed to the topmost muffle and then traverses one muffle after the other; *w, w* are working doors through which the blende is rabbled and pushed

forward. In this particular case the products of calcination are drawn off separately from each muffle. They escape through openings *a* in the rear wall of the furnace into vertical flues *b*, and thence through the main flue *S* to the sulphuric acid works. As above noted, this method of collecting the products of calcination has been discontinued, and they are now made to traverse the whole of the muffles, and escape from the uppermost one to the main flue. Such a furnace calcines in 24 hours about 4 tons of blende down to 0.6 to 1.06 per cent. of sulphur, consuming a quantity of good coal equal to 20 to 25 per cent. of the weight of the raw ore. Two men on a shift are sufficient to work the furnace. Recently this furnace has been improved by cutting each muffle into two by means of vertical walls across the middle, and so uniting the halves lying below each other by vertical flues that the blende has only to traverse these halves of the muffles that lie one above the other, in a downward direction, the calcination being in nowise injured thereby, although the blende only has to travel half as far as it had to in the older form. At the same time, with ores rich in sulphur, the two lowermost muffles alone are heated externally, the upper ones receiving only the heat generated by the oxidation of the sulphides. By these means the output of the furnace has been increased by 30 per cent., and the labour required has been diminished by 25 to 30 per cent. The flame takes the same course as previously. Furnaces of this construction are at work, for example, at the Guido Works, near Chropaczow, at the Silesia Works near Lipine, at the Recke Works near Rosdzin, at the Munsterbusch Works, and at the Rhenania Works, both near Stolberg.

The most recent furnaces have muffles 40 feet 9 inches long and 5 feet broad. Each muffle is divided by a partition into two divisions, each of which is 20 feet 4 inches long. The arch of the muffle is 9 inches high at the centre, and 5 inches at the sides. Each muffle has ten working doors, that is to say five for each half, which can be closed by cast-iron slides. The air employed for oxidation is heated in flues which lie beneath the lowest draught-flue. The construction of the furnace at the Guido Works<sup>1</sup> is shown in Figs. 52 and 53, in which *f* is a step-grate, the flame from which heats the two muffle divisions *e*, and the floor of the muffle divisions *d*, traversing the flues *g* and *h* into the flue *i* leading to the stack. The ores are dried upon the roof of the furnace, and are then charged through the openings *a, a* into the topmost muffle divisions *b, b*. Thence they pass into the divisions corresponding to each half of the furnace, *c, d* and *e*.

<sup>1</sup> *Berg- und Hüttenm. Ztg.* 1891, p. 450.

and after the calcination is complete are drawn out from the divisions *c*. The gases produced in calcination traverse the various muffles, and escape through the openings *k* from the topmost muffle into a main flue. There are two men on the shift, or four in 24 hours, during which time 5 tons of zinc blende are roasted with a consumption of coal equal to 20 per cent. of the weight of the raw ore.

At the Silesia Works, near Lipine, in the year 1895, a furnace of similar construction was calcining 5 tons of blende down to 1 per cent. of sulphur in 24 hours, with a consumption equal to 25 per cent. of inferior coal. The number of workmen in 24 hours was four, for calcining and firing, and  $\frac{1}{2}$  for charging the blende and delivering

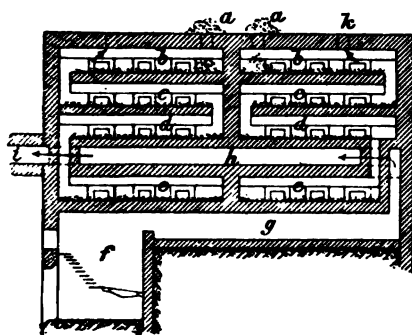


FIG. 52.

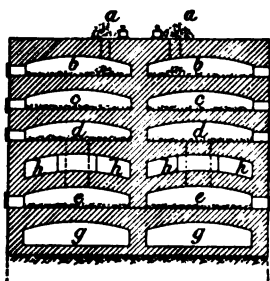


FIG. 53.

coal. The gases evolved during calcination contained 5 per cent. by volume of sulphur dioxide.

At the Recke Works, near Rosdzin, in Upper Silesia, in 1895, a furnace with 3 muffles, of which the lowest is heated by the flames from below, and the uppermost from above, calcines 3.5 tons of zinc blende in 24 hours down to from 1 to 1.5 per cent. of sulphur, 1.2 tons of coal being used. There are two men on a 12-hour shift. The gases evolved contain 6 per cent. by volume of sulphur dioxide.

At the Stolberg Works ores containing 27 to 28 per cent. of sulphur are roasted down to 0.5 to 1 per cent., when they are free from lime or magnesia; otherwise they retain 2 to 3 per cent. of sulphur. In 24 hours 8 tons of ore are calcined in a block consisting of a pair of furnaces, with a consumption of coal equal to 20 per cent. of the calcined ore. A crew of 4 men works the furnace block on each shift. The desulphurisation of blende and the formation of sulphate of zinc during calcination in the Hasenclever furnace of most recent construction is shown in the following table of analyses, which were executed at the Rhenania Works. A is uncalcined ore, Z is calcined

ore, 2 to 14 are the various samples taken during the process of calcination :—

Sample.	Zinc sulphide per cent.	Zinc sulphate per cent.	Zinc oxide per cent.
A . . . . .	57·2	0	0
2 . . . . .	53·5	3·5	0·8
3 . . . . .	53·0	3·8	3·4
4 . . . . .	48·4	4·2	4·6
5 . . . . .	39·9	4·3	12·3
6 . . . . .	35·2	5·0	16·5
7 . . . . .	34·8	6·0	17·0
8 . . . . .	25·2	6·3	27·1
9 . . . . .	24·2	5·2	30·0
10 . . . . .	19·2	5·8	32·6
11 . . . . .	10·0	7·8	40·0
12 . . . . .	7·9	6·2	44·9
13 . . . . .	1·5	4·7	52·5
14 . . . . .	1·6	2·6	53·0
Z . . . . .	1·2	0	55·0

The Hasenclever furnace has fairly established itself in the Rhine provinces and Silesia, and has there replaced the older Hasenclever-Helbig furnaces completely, and reverberatory furnaces in great part.

#### *Calcination in Fixed Muffle Furnaces with Machine Rabbling*

Such furnaces are employed with advantage in districts where the rate of wages is very high. They consist of muffle furnaces with some mechanical rabbling appliance which receives either a rotating or a reciprocating motion.

The Haas<sup>1</sup> furnace is a furnace with rotating rabbles. It is distinguished from the McDougall furnace described in Volume I, p. 69, by the chief difference that the separate circular muffles are not separated from each other by solid arches, but by hollow flues, through which the products of combustion can circulate. By means of the revolving rabbles the ore is successively drawn through four chambers, lying one beneath the other, and then reaches, if necessary, the floor of a rectangular muffle, which is the first to be heated by the flames, and in which the last portions of sulphur are removed from the blende. The construction of this furnace<sup>2</sup> is shown in Figs. 54 to 56, in which *a, a* are the four muffles, through the midst of which the shaft *x*, provided with rabble arms, passes. Each pair of muffles lying one above the other is connected

<sup>1</sup> D. R. Patent, No. 23080.

<sup>2</sup> *Berg- und Hüttenm. Ztg.* 1884, Plate I. Figures 12-34.

by means of the flues *b* for the products of combustion, and the vertical shafts *n* for the passage of the ore; *c* are flues communicating with the stack, and which consist of chambers between the individual muffles and of vertical flues which connect these chambers. The gases are generated in a producer, and pass through the flue *d* into the heating flues; they pass in the direction indicated by the arrows, and after they have heated the topmost muffle, escape through a

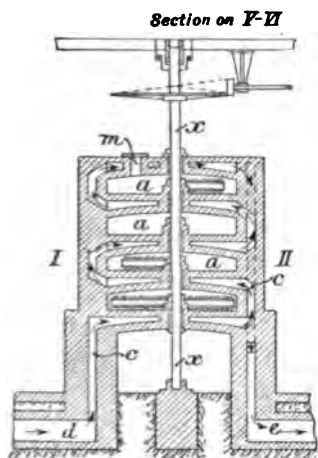


FIG. 54.

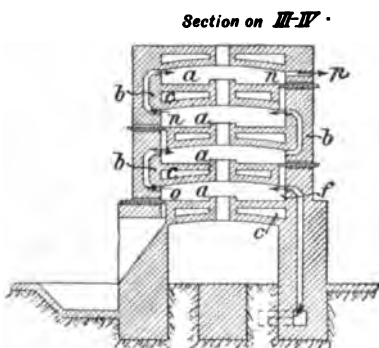


FIG. 55.

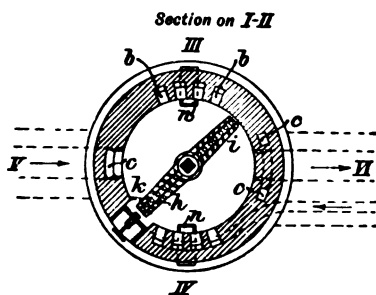


FIG. 56.

descending vertical flue into the horizontal flue *c*, which leads them into a regenerator for heating the air used for oxidation. The latter enters the bottom muffle at *f*, and traverses, together with the gases evolved, the whole of the muffles. These gases escape from the topmost muffle through the flue *p* to the works where they are to be utilised. The blende is charged into the topmost muffle through the shaft *m*, rabbled by the tines of the rabble arms, and gradually moved forwards towards the lower muffles. The shaft *x* can be turned to

the left as well as to the right, and has two cast-iron arms in each muffle. The individual tines *h*, fastened to one arm, are movable, whereas those carried by the other arm are fixed and are set obliquely. By means of the lever *k*, the tines *h* can be so placed that the pulverulent blende may be pushed either towards the centre or towards the circumference. When the ore from the upper muffle is to be transferred to the one next below it, the tines *h* are so placed that they push the ore towards the circumference. It then drops through the slot *n*, which can be closed by a slide when desired, into the muffle below, and thence subsequently in the same way into the next lower muffle, and finally into the last muffle. From the last muffle it is discharged similarly through the slot *o*. The discharged ore either drops into a vault or into a long rectangular muffle not shown in the figure, in which it is roasted dead. The products of calcination escape from this rectangular muffle into the bottom round muffle, and pass in the same direction as the gases developed in the latter. The flame first heats the rectangular muffle by means of various flues, and then passes into the flue *c* for the round muffles. The gases produced in this furnace contain from 6 to 7 per cent. by volume of sulphur dioxide. Such furnaces are in operation at Oberhausen for the calcination of blende containing on the average 25 per cent. of zinc.<sup>1</sup> The size of the grains should not be less than 0·08 inch. The hearths are 8 feet 2 inches in diameter, and the thickness of each floor amounts to 4 inches. From the bottom circular muffle the ore passes on to two hearths, lying one above the other, each 19 feet 8 inches in length, with 4 working doors in each, upon which it is roasted dead by means of hand labour. The gases from the muffles are employed for the manufacture of sulphuric acid. One workman is required for each furnace, the output of which is equal to 3·4 tons of blende per 24 hours. The consumption of coal for calcination amounts to 17 per cent. of the weight of the calcined ore, and for the production of power to 5 per cent. The calcined ore contains on the average 1 per cent. of sulphur.

At the works of Hegeler and Matthiesen, at La Salle, in Illinois, U.S.A., multiple calcining muffle furnaces with mechanical rabblers are in use. Such a furnace has 7 muffles, one above the other, each of which is 46 feet long and 4 feet 6 inches broad. The three lowermost muffles are heated by means of producer gas, the flame passing first below and then above them. Two furnaces are united to form one block. There is one rabble common to the two muffles which lie side by side. It is moved at intervals of an hour by means of a rod

<sup>1</sup> *Revue Univers. des Mines*, 1894, p. 38.

moved by friction wheels backwards and forwards through the blende spread out in the muffles. Such a double furnace calcines in 24 hours 23 tons of zinc blende, with a consumption of 4·8 tons of refuse coals.<sup>1</sup> In Fig. 57, *a* are the muffles and *b* the flues; *c* are flues through which air is conveyed to the muffles, and *d* the flues for introducing air into the fire-box.

The Rhenania Chemical Works at Stolberg has patented a Hasenclever furnace with mechanical rabblers.<sup>2</sup> This furnace consists of 4 muffles lying one immediately above the other, through which an endless chain provided with rabblers and scrapers at fixed distances apart, is kept moving. The rabblers stir the ore, whilst the scrapers move it forwards. The ore is charged into the topmost muffle, and then gradually transferred to the lower ones, until it is discharged from the bottom muffle in the calcined state. In order not to expose the endless chain to the flames there are no flues between the separate muffles. The flames, therefore, are carried round the muffles in one single flue. The description of the furnace as given in the Patent, 1892, page 321, resembles that of the O'Hara furnace, as described in Vol. I., p. 72. This furnace does not appear to have come into practical use as yet.

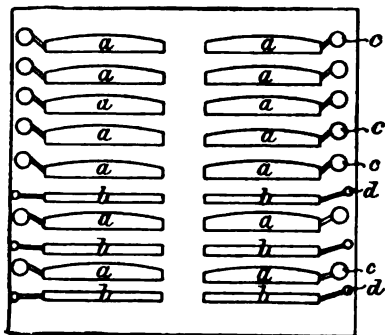


FIG. 57.

A muffle furnace built on the principle of the Brown furnace is worked successfully at the works of v. Giesche's Erben, at Rosdzin, in Upper Silesia.

The Falding furnace<sup>3</sup> in use at the works of the Mineral Point Zinc Company, Wisconsin, is shown in Figs. 58 to 60. The furnace is a double one, each half containing three hearths lying one above the other. The section through the hearths is shown in Fig. 58, the left half showing the arches upon which the hearths are laid, the right half the vertical shafts to which the rabble arms are fixed. Fig. 59 represents a longitudinal section through the middle of the furnace, and Fig. 60 a section through the fire-grate. Each hearth is 49 feet 6 inches long and 9 feet 10 inches wide. In each half of

<sup>1</sup> *The Mineral Industry*, 1894, p. 215.

<sup>2</sup> D. R. Patent, No. 61043.

<sup>3</sup> Ingalls, *The Metallurgy of Zinc and Cadmium*, p. 139.

the furnace there are seven upright hollow shafts bearing the rabble arms, and these are set in motion by a horizontal shaft in the arch underneath the hearths. The ore fed into the uppermost hearth is moved forward by the first rabble into the sphere of action of the second, thence into that of the third, and so forth until it falls through a slot at the end of the hearth, opposite to the charging-end, on to the next lower-lying hearth. This it traverses in the opposite direction, then falls on to the lowest hearth, is rabbled along this in the same direction as on the topmost hearth, and finally is discharged. The rabble arms are so arranged that no interference

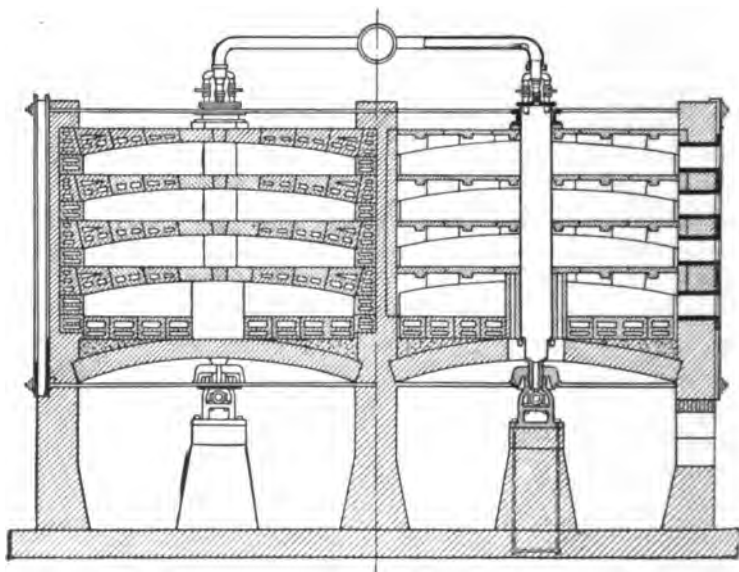


FIG. 58.

with one another can take place during their rotation. They are hollow, and are kept cool by air which passes through the hollow shaft.

Air for oxidation purposes is introduced into the furnace by means of a fan. In the side walls of the furnace there are doors, usually closed, which allow of the removal of worn-out rabble arms, and their replacement by new ones. Neighbouring rabble arms move in opposite directions so that the path of the ore in the furnace is sinuous. The hearths are built of thin bricks, which rest on arches of hollow brick (Fig. 58). The furnace has 4 fire-grates. Nothing is known as to the economic results of calcination with this furnace.



Another more recent muffle furnace with travelling rabble, like that of the Wethey furnace, has been designed by Wetherill.<sup>1</sup>

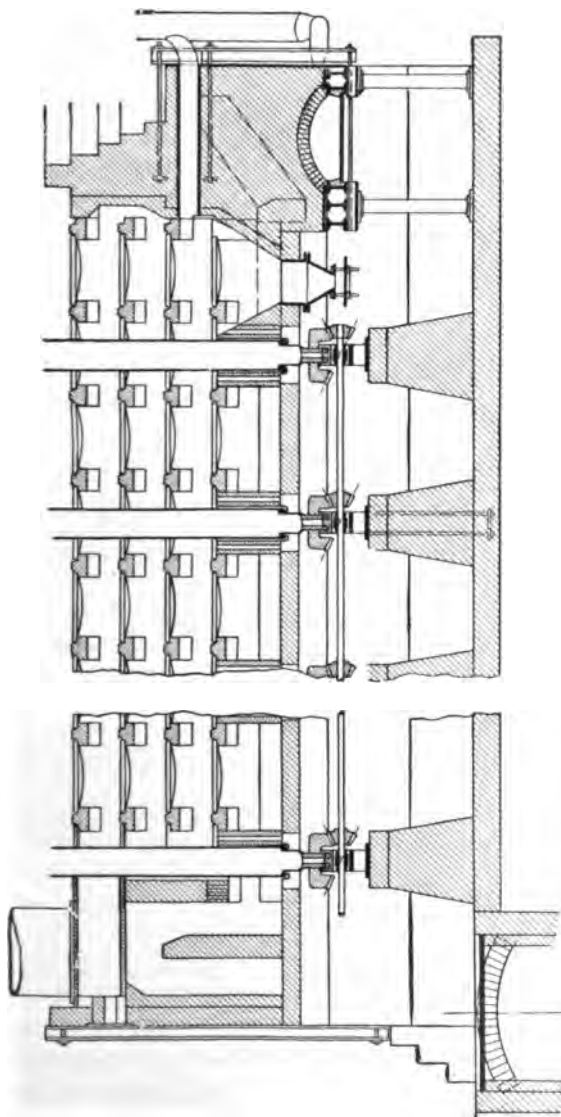


FIG. 59.

#### *Calcination in Furnaces with Movable Working Chambers*

These furnaces are formed by rotating cylinders in which the flame is kept separate from the ore. Such a furnace has been pro-

<sup>1</sup> U. S. Patent, No. 678078; July 9, 1901.

posed by Koehler in Lipine.<sup>1</sup> It consists of a rotating cylinder of cast- or wrought-iron, lined with firebrick, and fired with gas. In that portion of the lining which is nearest the interior of the furnace there are flues parallel to the axis of the cylinder traversed by the burning gases. In that portion of the lining nearest the outside of the furnace there are air flues running parallel to the heating flues. In the former, the air required for oxidation, which moves in the opposite direction to the products of combustion, is first heated, and

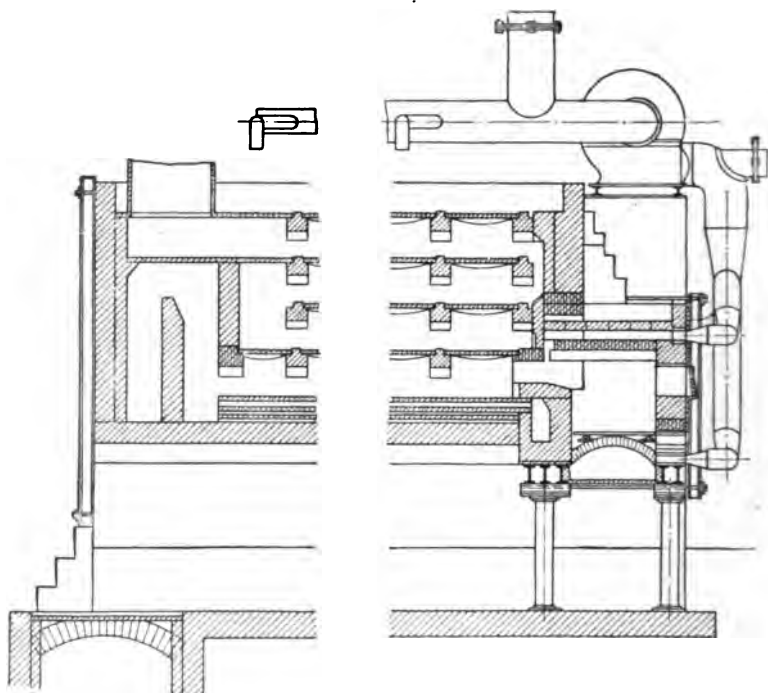


FIG. 60.

enters at one end of the cylinder through a tube lying in the axis of the furnace. The products of calcination escape at the opposite end of the furnace by means of another tube also lying axially. The zinc blende is automatically charged into the furnace by means of an apparatus attached to a hopper, and is automatically discharged at the opposite (hottest) end. The furnace is thus continuous-acting. In the interior of the furnace there are walls provided with apertures which divide the furnace to some extent into different chambers.

<sup>1</sup> D. R. Patent, No. 57522, May 7, 1890.

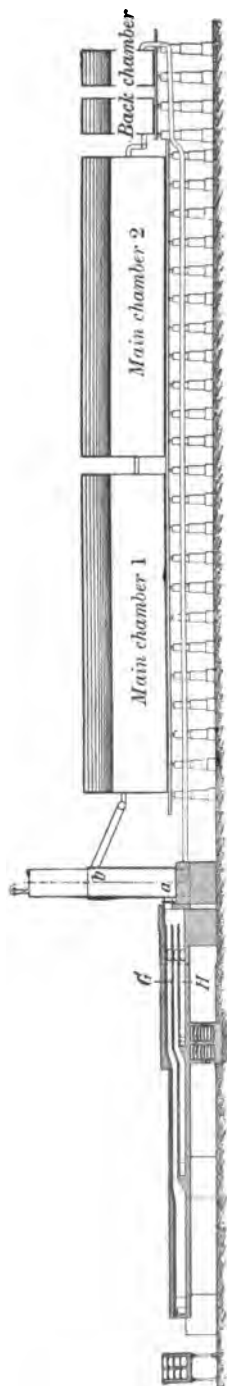
the object of which is to prevent the products of calcination, concentrated in the last chambers, from striking back. A furnace of this description, 24 feet 4 inches long, is in use at Lipine for the dead-roasting of blende; and another similar furnace, 36 feet 9 inches long, is used for the preliminary roasting of blende containing pyrites, with the object of converting the pyrites into magnetic oxide of iron. By the magnetic treatment of this calcined ore the greater part of the iron can be removed. Nothing is known as to the working of these furnaces. A rotating cylinder with the flues in the centre of the furnace—the Douglas furnace—has also been proposed for the calcination of sulphide ores. It is described and figured in Vol. I., page 108.

### UTILISATION OF THE PRODUCTS OF CALCINATION.

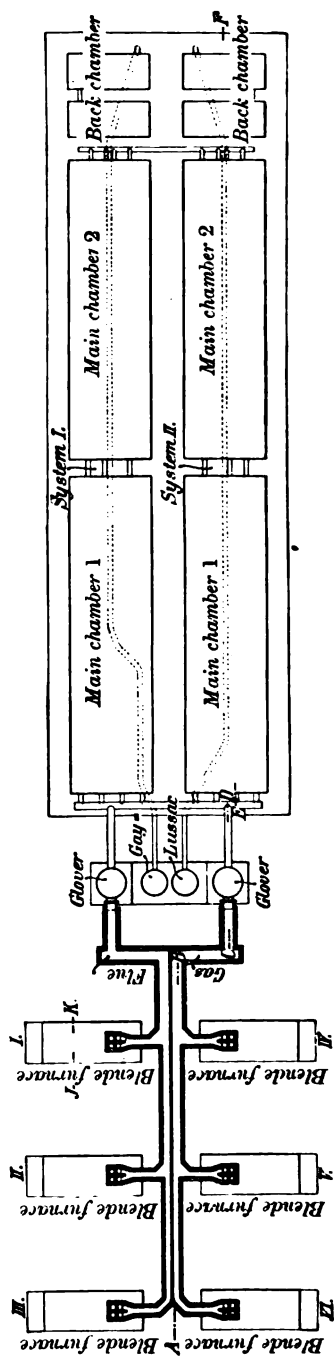
The products of muffle calcination have up to the present, with but few exceptions, been used exclusively for the production of English sulphuric acid, the method of manufacture of which may be taken as known. They may also, however, be used for the preparation of sulphuric anhydride, of fluid sulphur dioxide, of sodium sulphate, of sulphuretted hydrogen, of sodium hyposulphite, of sulphur, and for the solution of copper. The preparation of these bodies, with the exception of the sulphur, can only be carried out with advantage under certain local conditions, on account of the small demand.

When the products of calcination are to be used for the preparation of chamber acid, three Hasenclever double furnaces are united in one chamber system, efficient draught being provided for by leading the gases from each furnace through separate flues into the Glover tower. These flues are built close together, and unite just before entering the Glover tower (Fig. 61). To protect the workmen from injury by heat, passages 12 yards wide are left between the furnaces.

The Glover towers are filled with pressed bricks known as clinker, which rest on a grating of sandstone blocks; they are placed close to the Gay Lussac towers in order to facilitate their working and supervision. The chamber system comprises two main and two secondary chambers, and the gases pass through these in the order stated, escaping from the last secondary chamber into the Gay Lussac tower through a long lead pipe. From the Gay Lussac tower they escape into the open through a vertical pipe. Two systems, each of 255,000



**FIG. 61.**



**Fig. 62.**

cubic feet capacity, with corresponding calcining furnaces, are represented in Figs. 61 to 64.<sup>1</sup> The sides of the chambers are covered with wood, and the tops are roofed with tiles as a protection against change of temperature and destruction by weathering. The cross-section of the chambers is six-sided, for this economises lead and allows of a better utilisation of the chamber space and easier access to the chamber coverings. The weight of the chambers and their contents is borne by stone pillars. The draught in this system is produced by the outlet pipes of the Gay Lussac towers. In other works it is derived from chimneys. Fans are used for this purpose in the United States, and the yield of acid (60° B.) is said to be increased thereby up to 25 lbs. in 24 hours per 100 cubic feet of chamber space. The waste gases contain from 4 to 8 per cent. of oxygen in Germany; in Prussia they are not allowed to contain more than 1 oz. of sulphur trioxide in 120 cubic feet. The capacity of these chamber systems varies

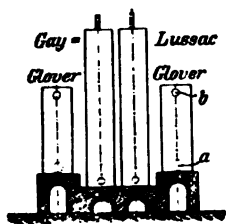


FIG. 63.

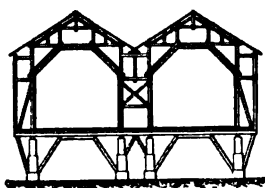


FIG. 64.

between 35,000 and 42,000 cubic feet; those described in the figures have a capacity of 255,000 cubic feet. All but the small systems can be worked with satisfactory consumption of saltpetre.

In recent times the gases obtained by roasting zinc blende in muffles have been used in the preparation of sulphuric anhydride and of concentrated and English sulphuric acid by the contact process.

Sulphuric anhydride was first manufactured by Winkler at the Mulden Works near Freiberg, from the products of calcination of pyritic lead and silver ores. The products of calcination were first led into lead chambers filled with fragments of coke, of burnt clay or of quartz, over which concentrated sulphuric acid trickled, and then passed through iron vessels heated externally, and containing inside platinised asbestos. The object of the first portion of the process was the removal of water vapour, whilst by means of the catalytic action of the platinum, sulphur dioxide and oxygen united to form sulphur trioxide. The gases carrying sulphuric anhydride were led

<sup>1</sup> *Chem. Industrie*, 1899, No. 2.

into towers in which concentrated sulphuric acid trickled down, so as to absorb the anhydride, which was distilled off from the solution of anhydride in sulphuric acid thus produced. The gases escaping from the absorption towers still contained the sulphur dioxide which had not been converted into sulphuric anhydride, and these were then conducted into lead chambers for sulphuric acid manufacture. By the use of this process only half the sulphur dioxide at most was converted into anhydride.

It has been shown by recent investigations that it is possible to convert 95 per cent. of the sulphur dioxide into trioxide by careful regulation of the temperature, purification of the gases from harmful constituents, and by proper arrangement of the contact apparatus and choice of a suitable contact substance. The gaseous products of calcination are scrubbed, dried, led into the contact apparatus, and on issuing therefrom are absorbed by sulphuric acid. This arrangement allows of the preparation of acid of any desired strength. As, however, sulphuric anhydride has but a limited application, concentrated sulphuric acid from 66° B. and upwards is generally prepared. The passage of the gases through the various parts of the plant must be brought about by blowing or exhausting fans. The contact process is more expensive as yet than the chamber process. Finely-divided platinum, in Freiberg, platinised asbestos, is used as the contact substance. Winkler's Patent (1878) is "for the chemical transference of contact reagents to bulky bodies, inactive in themselves, in a manner similar to the dyeing of the fibres of a fabric." The Zinc Industrial Society, formerly Wilhelm Grillo and Schröder,<sup>1</sup> use soluble salts of the alkalis and the alkaline earths, and metallic salts generally, as carriers of the platinum. The contact substance is prepared by mixing solutions of the salts in question and platinum salts, evaporating the solution to dryness, and breaking up the crusts which form into grains of approximately the same size. The dust which is formed in this process is re-dissolved, and the solution treated as before until all the material has been brought into granules of suitable size. It is then brought into the contact apparatus and heated, whereby the platinum salts are decomposed and the platinum is left in a state of very fine subdivision. The preparation of concentrated sulphuric acid from zinc blende by this process is in use at Hamborn in Bergisch-Gladbach, at Lipine in Upper Silesia, and at Mineral Point in the United States.

Fluid sulphur dioxide is manufactured from the products of calcination of zinc blende in muffles, at the zinc works at Hamborn

<sup>1</sup> D. R. P., Nos. 102, 244.

near Oberhausen, and the Silesia Works near Lipine. Having regard to the still restricted applications of fluid sulphur dioxide (for the manufacture of sulphite cellulose, for the production of cold, for the manufacture of sugar, and for bleaching), and to the great expenses entailed by the plant for its manufacture, it is not to be expected that its production from the products of calcination will be much extended in the immediate future. At the Guido Works, near Chropaczow, in Upper Silesia, where the process had been in use for some considerable time, it has lately been stopped, sulphuric acid works being in course of erection there. The process employed was invented by Schröder and Hänisch. As it separates gaseous sulphur dioxide from the gases evolved from the muffle furnaces in a condition of great concentration, in which it may also be employed for other purposes, it deserves somewhat fuller consideration. The process<sup>1</sup> consists in absorbing sulphur dioxide out of the gases by means of water trickling through a coke tower, in expelling from this water the sulphur dioxide in a concentrated state mixed only with a small amount of water vapour by means of heat, in separating the moisture from the mixed gases by means of concentrated sulphuric acid or calcium chloride, and in condensing the concentrated gaseous sulphur dioxide thus obtained by means of a compressor. This process does not admit of the preparation of concentrated sulphur dioxide from the gases of reverberatory furnaces with advantage; it can only be produced from gases which contain at least 4 per cent. by volume of sulphur dioxide, such as are evolved from shaft furnaces and muffle furnaces. As regards the execution of the process, the absorption of the sulphur dioxide is performed in coke towers through which water trickles. The sulphur dioxide is expelled from the water in three forms of apparatus, in which the heat of the products of calcination in part, and in part the latent heat of water vapour which is developed when the sulphur dioxide is expelled from the water containing the latter, in part the residual heat of the water freed from sulphur dioxide, are all utilised. The acid water is first conveyed into a system of low lead chambers in which it is warmed by means of the water from which the acid has been driven off, which surrounds these chambers. Thence it passes into closed leaden tanks under which circulate hot gases as they escape from the furnace before they pass into the absorption tower. The heat which they give off to the tanks raises the fluid contained in the latter to the boiling point. The sulphur dioxide escapes, in consequence, from the boiling solution and enters the dehydrating apparatus. The boiling fluid,

<sup>1</sup> D. R. Patents, Nos. 26181, 27581, and 36721.

not, however, quite free from acid, is drawn off from the leaden tanks into a so-called *colonne*, in which the last portions of sulphur dioxide are removed from it by the direct action of steam, the steam being separated from the sulphur dioxide by means of a spray of cold water. The hot water, now free from acid, is used for heating the acid water as it first escapes from the absorption towers, by allowing it to escape from the *colonne* through a system of lead chambers which surround the lead chambers containing the acid water. Water vapour is best separated from the sulphur dioxide which has been driven out of the water by allowing the gaseous mixture to ascend through a tower filled with coke, down which concentrated acid is trickling, which absorbs all the water. The sulphur dioxide, thus completely dehydrated, is compressed to a liquid by means of a force-pump made of bronze, and is collected in iron vessels of sufficient strength. The pressure that has to be employed varies according to the season from 2 to  $3\frac{1}{2}$  atmospheres. The intermixed, difficultly compressible gases are allowed to escape into the absorption tower by means of a valve placed in the receiver. The fluid sulphur dioxide is shipped in iron vessels. It contains 99.8 per cent. of pure  $\text{SO}_2$ . The gases evolved from the calcination of zinc blende at Hamborn and Lipine contain about 6 per cent. by volume of sulphur dioxide; in the absorption tower this is removed from the gases down to 0.05 per cent. by volume. The water which flows out from the towers contains 12 pounds of sulphur dioxide in 100 gallons.

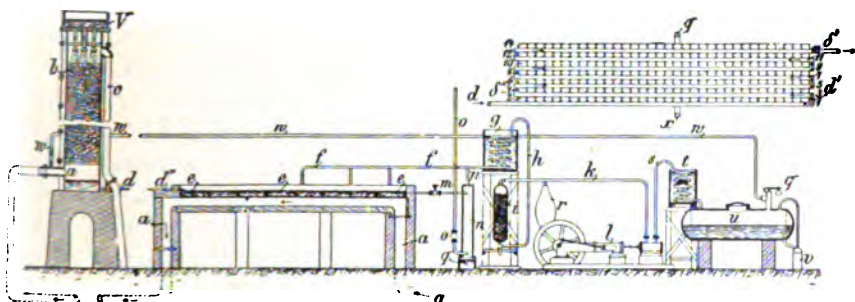
The construction of the plant for the production of fluid sulphur dioxide from the products of calcination is shown in Fig. 65.<sup>1</sup>

The gases pass from the calcination furnace through the flue *a* into the absorption tower *b*. On their road to the latter they give off their heat to the leaden tanks *c*. They ascend in the lead tower filled with coke and are freed from their sulphur dioxide by means of water coming from the distributor *V*. The gases that reach the top end of the tower, consisting of nitrogen, oxygen, and very minute quantities of sulphur dioxide, are conveyed by the descending tube *c* into the stack. The water containing sulphur dioxide in solution escapes from the pipe *d* at the foot of the tower first into a heating apparatus, which is omitted in Fig. 65, but is shown separately in Fig. 66. It consists of a series of flat leaden chambers each 16 inches deep, disposed one above the other, these lead chambers forming two systems. In the one system the solution which is to be warmed ascends, whilst in the other system the hot water

<sup>1</sup> *Zeitschr. f. Angewandte Chemie*, 1888, p. 448; Lunge, *Soda Industrie*, vol. i. p. 264.



descends, giving off its heat to the ascending fluid. For this purpose the chambers are so arranged that a chamber of the one system alternates regularly with one of the other. In the chambers marked with odd numbers, 1, 3, 5, 7, 9, 11 and 13, the acid solution is ascending, whilst in the chambers with even numbers, 14, 12, 10, 8, 6, 4 and 2, the hot water is flowing down. The adjacent chambers of each system are so united with each other that the combination takes up the whole side of the chamber. The individual chambers are stayed by means of strips of lead made fast inside them, these lying in the direction of the flow of the solution. The acid water escaping from the absorption tower enters at *d* into chamber No. 1, rises at *d'* into chamber No. 2, at *d''* into No. 3, and so on, till it escapes at *d'* from the last chamber 13 in a heated state, entering the leaden tanks *e* at *d''*. The hot water passes in the opposite direction.



FIGS. 65 and 66.

It enters the topmost chamber 14, through the tube *q*, flows through it and passes from the end of it by a tube not shown in the figure into the chamber 12; from this into No. 10, and so on until it escapes at the end of chamber No. 2 through the tube *x* after having given off the greater portion of its heat. The acid solution which has thus been warmed passes through the tube *d''* into the leaden tanks *e*, which it traverses one after the other. It is here heated to boiling point by means of the hot products of calcination passing underneath the tanks, and in consequence gives off sulphur dioxide mixed with a certain amount of water vapour. This gaseous mixture flows through the tube *f* into the water-cooled worm *g*, in which a portion of the water vapour is condensed; thence it flows back through the above-named pipe into the tanks or into the *colonne*, and thence through the tubes *h* into the drying tubes *i*, in which the last portion of the water vapour is retained by means of coke soaked in concentrated sulphuric acid. From the drying chamber the sulphur

dioxide passes through the tube *k* into the compressor. In order to regulate the pressure a silk bag *r* is interposed in the tube *k*. According to the size of this bag the movement of the pump *l* is regulated. The gas is forced through the tube *s* into the worm *t* in which it is liquefied. The liquid sulphur dioxide flows out of the worm into a wrought iron tank *u*. The gases, oxygen and nitrogen, which are carried with the fluid, escape when the valve *q* at the top of the tank is opened into the tube *v*, which leads them to the absorption tower. The fluid sulphur dioxide is drawn off from the tank into wrought iron cylinders *v* holding 110 or 120 lbs., or else into tank wagons holding 10 tons.

The boiling solution that remains behind in the tank *e* contains a small quantity of  $\text{SO}_2$ ; to extract the latter it is run through the tube *m* into the *colonne* *n*, where it is raised to boiling by means of vapour entering from below through a tube *o*, whilst water is sprayed into the upper end. The sulphur dioxide and the steam rise in the tower, are in part condensed by the water trickling down, and expelled again when the latter reaches the bottom. Of the gas escaping from the upper end of the *colonne*, the steam is condensed by the water spray and flows down with the latter. A portion of the sulphur dioxide is here absorbed by means of this water. As the quantity of the latter only suffices for the absorption of a relatively small proportion of the sulphur dioxide, the greater portion of the gas escapes from the tube *p* into the worm *g*, and there unites with the gas evolved from the tanks *e*. The solution trickling down in the *colonne* gradually loses its sulphur dioxide as it is raised to the boiling point by the steam, and thus reaches the bottom of the *colonne* free from sulphur dioxide; thence it escapes through the tube *q* into the above-described lead chambers and warms the acid water coming from the absorption towers. The *colonne*, which consists of a tower, the lower portion of which is filled with circular tiles and the upper portion with coke, has recently received certain improvements.<sup>1</sup> It is shown in Fig. 67 (D. R. P. 36721). The hot steam enters at *a*; a water-spray is produced by the rose *b*; through the tube *d* sulphur dioxide escapes; through the tube *e* the solution escapes after it has been freed from acid and has been heated to the boiling point. By means of the circular tiles, the solution that is trickling down is delayed, and thus better exposed to the action of the ascending steam. The cylinders in which fluid sulphur dioxide is sent into the market are shown in Figs. 68 and 69. They have a screw valve *c* which is protected by the cap *a* when they are being

<sup>1</sup> D. R. Patents, Nos. 36721, 52025.

transported. If sulphur dioxide is to be employed in the gaseous form the bottle is placed vertically (Fig. 68). The spindle of the screw valve *c* is turned by means of a key and opens the pipe *b*; through the latter gaseous sulphurous acid then escapes and continues to do so until the temperature, in consequence of the evaporation of the liquid, falls to  $-10^{\circ}\text{C}$ . A further quantity of gas can then only escape when the cylinder has taken up from its surroundings the requisite quantity of heat. If the sulphur dioxide is to be utilised in the fluid state the cylinder is laid down so that the small tube *b* is uppermost (Fig. 69). By means of the pressure of the gas, fluid sulphur dioxide is then forced out through this tube. The whole contents of the bottle can be expelled by means of the bent tube *n* which reaches to the bottom. To safeguard against explosions the cylinders are tested to a pressure of 50 atmospheres. The vapour tension of sulphur dioxide amounts at  $10^{\circ}\text{C}$ . to 1.6 atmospheres; at  $20^{\circ}$  to 2.4; at  $30^{\circ}$  to 3.51, and at  $40^{\circ}$  to 5.15 atmospheres. These bottles are best preserved in some locality where the temperature does not exceed  $40^{\circ}\text{C}$ .

Sulphur dioxide evolved from muffle furnaces is also suitable for the preparation of sodium sulphate from common salt, according to the process of Hargreaves, which has been practised in a

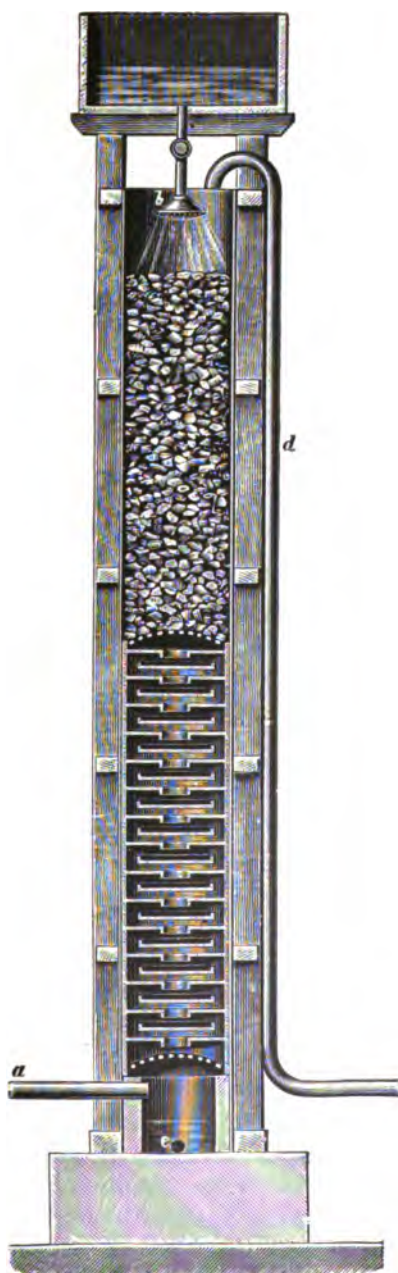


FIG. 67.

number of English soda works, and since the year 1890 at the Rhenania Works. It consists in leading the products of calcination mixed with air and water vapour into a cast-iron cylinder heated externally, inside which spherical pieces of salt are arranged upon an iron grating. Sodium sulphate is thus formed with the evolution of hydrochloric acid.

These sulphurous gases are also available for the production of sulphuretted hydrogen by passing them, mixed with water vapour, through shaft furnaces filled with glowing coke, which is kept at a red heat by passing air from time to time over it. Sulphuretted hydrogen forms in accordance with the equation:—



Sulphuretted hydrogen is, however, used but rarely, and only in limited quantities, for the precipitation of metals such as copper and silver from their solutions,



FIG. 68.



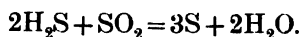
FIG. 69.

so that there is no probability that this process will be introduced into blende calcining establishments.

Sodium hyposulphite (thiosulphate) can be produced from these gases by passing them through a solution of sodium sulphide, the salt being formed and sulphur produced simultaneously. Its employment for the extraction of silver is, however, a very limited one, so that the utilisation of the products of the calcination of blende for this purpose does not seem practicable.

Although there is a large demand for sulphur, its production from the gases evolved from muffle furnaces is tolerably expensive, and has not, therefore, been conducted on a large scale. It can be produced from these gases directly by passing them into solutions of the polysulphides of sodium or calcium, and by allowing the gases to act upon sulphuretted hydrogen, or indirectly by first separating out the sulphur dioxide and reducing the latter by carbon or coal gas. Polysulphides of the alkaline earths will only be used for the manu-

facture of sulphur when they can be obtained free of cost as the noxious bye-products of other processes, such as the decomposed residues from Le Blanc soda works. By means of sulphuretted hydrogen, sulphur can be obtained from the products of calcination by allowing both gases to ascend through wooden towers in which a solution of calcium chloride is trickling down, sulphur being formed in accordance with the equation :—



The gases are introduced at the bottom of the tower, whilst the solution of calcium chloride which causes the sulphur to separate out enters at the top and trickles down the tower, flowing over wooden plates inclined alternately in opposite directions. The sulphur, which is thrown down upon these boards, escapes with the solution of calcium chloride from the towers into a series of vats placed one below the other, in which it is deposited, whilst the clear solution is pumped up to the top of the towers to be used over again. The sulphur is melted according to Schaffner's method under water by means of steam at  $2\frac{1}{2}$  atmospheres pressure. Sulphuretted hydrogen can be produced (unless it is available as a bye-product of certain processes) as described above, viz., by leading a portion of the products of calcination, together with water vapour, through a column of red-hot coke. It may also be produced according to Chance's method, by treating residues from the Le Blanc soda works with carbon dioxide. This process can only be recommended when sulphuretted hydrogen is available without any great expense.

Sulphur can only be produced by the reduction of sulphur dioxide by carbon when the gases are in a concentrated form, such as are employed for the manufacture of the fluid sulphur dioxide according to the Schröder and Hänisch process. It cannot, therefore, be produced direct from the gases from muffle furnaces, but only after a previous concentration of the latter by the aid of water. In the earlier experiments for the production of sulphur from the diluted gases a portion of the carbon was burnt to waste by the action of the air contained in the gases; moreover, in consequence of the dilution of the sulphur dioxide by indifferent gases, its reduction to sulphur was only very imperfect. The extraction of sulphur from the sulphur dioxide concentrated as above described has been patented by Schröder and Hänisch. The concentrated sulphur dioxide is first passed through a muffle filled with red-hot coke, and then through a second vertical muffle which contains red-hot indifferent bodies known as "intact bodies," such as

firebricks and burnt clay. In the muffle filled with coke about half the sulphur dioxide is reduced to sulphur, whilst in the second muffle the sulphur dioxide which still remains and the gases formed in the first muffle, viz., carbon monoxide, carbon bisulphide, and carbon oxysulphide, act upon each other, the products being carbon dioxide and sulphur. The sulphur vapours and carbon dioxide escape from the second muffle into a condensing chamber in which the greater portion of the sulphur is deposited in the fluid state, and a small portion as flowers of sulphur. In some experiments tried at the Grillo Zinc Works 99 per cent. (by volume) of the sulphur dioxide was

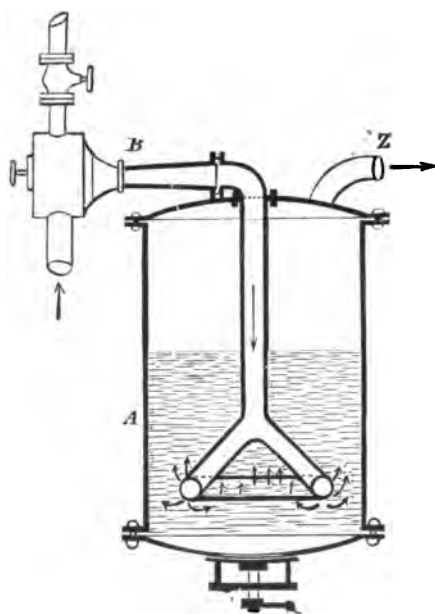


FIG. 70.

thus reduced to sulphur. The gases escaping from the condensing chamber contained 96 to 97 per cent. by volume of carbon dioxide, and 2 to 3 per cent. of carbon monoxide. According to the patents of Schröder and Hänisch, the reduction of sulphur dioxide can also be performed by means of carbon monoxide, coal-gas, or any other gas rich in carbon. As to the economic results obtained by the extraction of sulphur in the above manner no opinion can be given at the present time, as the process has not been carried out on a large scale. The concentrated sulphur dioxide produced by means of water has

hitherto been used exclusively for the production of fluid sulphur dioxide.

The utilisation of the gases from muffle furnaces for the dissolving of copper is only possible under special local conditions, and even then on a very small scale, as, for example, for the extraction of copper from poor oxidised or acid copper ores, or for dissolving copper from cement copper containing gold or silver. In the first case the gases produced in calcination, together with water vapour and nitrous gases, are allowed to act upon the ores lying upon a grating composed of stone or wood. In the second case Rössler's arrangement may be used. This is shown in Fig. 70, and consists of a vessel

of wrought iron *A*, containing a solution of sulphate of copper. By means of a Körtling injector *B*, the gases are forced in fine jets through a ring into the solution. The sulphur dioxide is thereby converted into sulphuric acid, the sulphate of copper being at the same time reduced to cuprous sulphate. The sulphuric acid thus formed dissolves the cement copper containing gold and silver, the latter metals being left behind. Nitrogen and oxygen escape through the tube *Z*. This arrangement is employed at the parting works in Frankfort-on-the-Main, where the gases which contain the sulphur dioxide are produced by the solution of auriferous silver in boiling concentrated sulphuric acid. The furnace gases may also be allowed to act on moistened iron as in Winkler's process for the preparation of iron vitriol.

## 2. THE PROCESS OF REDUCTION, OR THE EXTRACTION OF ZINC FROM THE CALCINED ORES

The reduction of zinc from the calcined ores is performed by heating the latter with carbon to a white heat in fire-clay vessels. Zinc is then separated in the form of vapour and is collected in clay vessels known as receivers or adapters. The process of reduction is therefore a process of "compound volatilisation" or of distillation. The ores which are to be subjected to this process contain zinc in the form of oxide or silicate. In consequence of the imperfect calcination of zinc blende, small quantities of zinc may be present as sulphide or sulphate. In the presence of iron any sulphur is combined with this metal. Of foreign bodies, the calcined zinc ores contain oxides and silicates of iron and manganese, sulphide of iron, lead oxide, sulphate and silicate, silicates of alumina, quartz, calcium and barium sulphates, antimonates and arseniates, lime, magnesia, cadmium oxide and silver. Zinc is reduced from its oxide both by carbon and carbon monoxide. By its reduction by carbon, carbon monoxide is formed, which again reduces more zinc, with the formation of carbon dioxide. In what proportion the carbon monoxide contributes to the reaction is not known. In any case the carbon dioxide produced is immediately reduced to carbon monoxide by the excess of carbon present, so that it has no opportunity of re-oxidising the zinc vapours. It is only when carbon is deficient that the carbon dioxide can re-oxidise the zinc at a red heat. The fact that the gas escaping from the reducing apparatus after the commencement of distillation really

only contains very small quantities of carbon dioxide is proved by the following analyses <sup>1</sup>:—

## GASES FROM RETORTS, LETMATHE.

	1	2	3	4	5
Carbon dioxide . . .	0.48	1.06	0.11	1.10	0.82
Carbon monoxide . .	not det.	92.16	97.12	not det.	98.04
Hydrogen . . . . .	5.32	1.83	not det.	„	0.72
Nitrogen . . . . .	not det.	1.01	0.41	„	trace

The gases of column 5 escaped immediately before the end of the distillation. Before the commencement of distillation the gases contained a considerable quantity of carbon dioxide and hydrogen, as also a certain amount of methane, as is shown by the following analysis <sup>2</sup>:—

Carbon dioxide . . . . .	15.58
Carbon monoxide . . . . .	38.52
Methane . . . . .	4.17
Hydrogen . . . . .	41.70
Nitrogen . . . . .	trace

The methane and a portion of the hydrogen are produced by the gases evolved from the lean coal, which is used as reducing agent. Another portion of the hydrogen is derived from the decomposition of the water vapour, contained in the charge, by the red-hot coal. This decomposition also produces a portion of the carbon dioxide and monoxide. Another portion of the oxides of carbon is produced by the action of the air still present in the vessel upon the carbon. The gases which escape from the muffles in the process of reduction at the Munsterbusch Works, near Stolberg, show the following composition:—

	1	2
Carbon dioxide . . . . .	0.09	0.11
Carbon monoxide . . . . .	95.36	97.42
Hydrogen . . . . .	3.72	1.20
Nitrogen . . . . .	0.61	0.92

Zinc can only be reduced from its silicate by solid carbon with the formation of carbon monoxide.

The zinc vapours escape, together with the gases formed during reduction, from the vessels into an adapter in which they are condensed, whilst the gases escape either direct into the air or into arrangements in which metallic particles carried off by them may be deposited. Any zinc present in the form of sulphide is not attacked by carbon, and therefore remains in the residues after distillation. Only in case the ores contain considerable quantities of

<sup>1</sup> *Dingl. Polyt. Journ.* 237, 390 (Fischer); *Berg- und Hüttenm. Ztg.* 1880, 371.

<sup>2</sup> *Ibid.*



iron oxide or basic silicate of iron is iron reduced from these substances by the carbon, the iron reducing any sulphide of zinc to metallic zinc. The formation of sulphide of iron is not, however, desirable, because it destroys the vessels used for distillation.

Any *sulphate of zinc* present in the ore is principally reduced to sulphide, which behaves just like the sulphide of zinc which has remained undecomposed on the calcination of the blende.

*Ferric oxide* is reduced to ferrous oxide and forms slags with any silica that may be present or with acid silicates. Ferrous silicates combine with any other silicates that may be present to form easily fusible double silicates. They also have the property of dissolving the silica and silicates contained in the material of which the vessels are composed, and thus contribute to the perforation and rapid destruction of these vessels. They also envelop portions of the charge and thus cause any zinc contained in these portions to be retained in the residues. Basic iron slags have the especial property of taking up oxide of zinc and thus withdrawing it from reduction. Lastly, in the absence of silica, metallic iron is reduced from basic iron slags, as also from oxide of iron. Such metallic iron decomposes any other sulphides that may be present, with the formation of sulphide of iron.

*Oxide of manganese* is reduced by carbon to manganous oxide, which forms with silica a very fluid slag. The latter would also envelop portions of the charge. The presence of manganous oxide or silicate tends to the destruction of the vessels, on account of the formation of readily fusible double silicates.

*Sulphide of iron* is not affected by the processes of reduction. It has an especial injurious action in that it perforates the walls of the vessels.

*Oxide of lead* is reduced to metallic lead, which is partly volatilised and goes with the zinc into the adapters, and partly remains in the residues. As long as it is not present in too great quantities, and as long as there are only reducing gases present in the retorts, the danger of the formation of silicate of lead, involving the rapid destruction of the walls of the retorts, is not great on account of the ready reducibility of the oxide of lead. If, however, there are large quantities of oxide of lead in the charge, a portion thereof may still remain unreduced at the temperature at which the formation of slag commences, and thus form a silicate. The same action may take place even when lead oxide is present only in small quantity if a considerable amount of air is allowed access to the retort during the course of the distillation. The opinion was formerly held that even

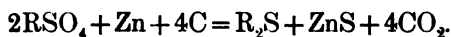
small quantities of lead—2 per cent.—cause the rapid destruction of the walls of the retort; but at present it has been proved that the presence of lead in the charge up to 8 per cent. does not notably affect the durability of the retorts. For instance, at Ampsin (Laminne Works) and at Corphalie, ores with 5 to 8 per cent. of lead and 52 per cent. of zinc, and at Bleiberg with 5 to 8 per cent. of lead, are being treated with good results. The retort residues, which contain up to 9 per cent. of lead in the form of small globules, are ground under edge runners, and then jigged, whereby the percentage of lead is brought up to 39. At the Wilhelmine Works, near Schoppinitz, ores with 10 per cent. of lead have been treated without affecting the durability of the muffles. The quantity of zinc left in the residues will be greater the lower the temperature, that is the more the lead that is not slagged off.

*Lead sulphate* is reduced to sulphide, which may react with iron reduced from oxide of iron, so that the greater portion of the lead is separated out, with the formation of sulphide of iron. Any sulphate of lead that has not been reduced may be converted into silicate of lead by the action of silica. Silicate of lead has a corrosive action upon the walls of the vessels. In the presence of any ferrous oxide reduced from ferric oxide, carbon may reduce lead from it, with the formation of ferrous silicate, which also has a destructive action upon the walls of the vessels.

*Silicates of alumina* have no injurious effect on account of their infusibility as long as other bases are not present. In the presence of bases such as the oxides of iron, manganese and calcium, easily fusible double silicates are formed, which envelop a portion of the charge and attack the walls of the vessels.

*Quartz* has no injurious action by itself, but if bases such as ferrous oxide, lime and manganese oxide are present, which form easily fusible silicates, it combines with them to form slags, which both envelop a portion of the charge and attack the vessels.

*Calcium and barium sulphates* are reduced by carbon to their respective sulphides, which tend to retain zinc in the residues from the distillation. According to Thum,<sup>1</sup> these substances appear to give off half their sulphur to the zinc in the presence of free zinc and carbon, in accordance with the equation:—



Other metallurgists, however, think that the presence of these sulphates brings about no loss of zinc. Thus Sander<sup>2</sup> found at

<sup>1</sup> *Berg- und Hüttenm. Ztg.* 1876, p. 154.

<sup>2</sup> *Ibid.* 1902, p. 466.

Chaudfontaine, in Belgium, that the residues from the distillation of calcined blende containing 9 per cent. of heavy spar did not contain more zinc than those obtained from material free from heavy spar. According to the same authority, calcium sulphate in quantities up to 10 per cent. does not promote the retention of zinc by the distillation residues. More experiments are needed to settle this question.

*Antimoniates* are partly converted into antimonides and partly are reduced to antimony, which is volatilised and may pass into the zinc. Sulphide of antimony is decomposed by iron with the formation of metallic antimony and sulphide of iron. *Arseniates* are partly reduced to arsenides, whilst in part arsenic is volatilised from them. A portion of the volatilised arsenic passes into the zinc.

*Lime* is only injurious in the presence of silica and oxide of iron, these substances tending to produce fusible silicates, the injurious action of which has already been pointed out.

*Magnesia* alone has no injurious effects, but in the presence of silica and oxide of iron likewise tends to form a slag. The presence of considerable quantities of magnesia tends to make the slag difficultly fusible, and thus prevents the absorption of zinc by the latter.

*Cadmium oxide* is reduced to cadmium and volatilised. Cadmium is more readily reduced and volatilised than zinc, and is therefore deposited with the first condensed pulverulent mixture of zinc and oxide of zinc. It is extracted from this powder.

Any *silver* contained in the charge is only volatilised in very small quantities. The greater portion of it remains in the distillation products, from which it can be obtained by smelting with lead.

### *The Charge for the Process of Reduction.*

The charges are prepared by mixing or grinding the ores with the coal used for reduction, no fluxes being added. Formerly lime used to be added to silicate of zinc. It was found, however, that this addition tended to the formation of easily fusible double silicates in the presence of other bases, and has therefore been discontinued. If there are various classes of zinc ore on hand, these should be so combined that a purely siliceous or a purely basic grade is obtained as far as possible. If this is not feasible, they must be so mixed that the silica and the bases shall form a slag as difficultly fusible as possible at the reduction temperature of the zinc, as in the case when large quantities of lime, or, better still, of lime and magnesia, or of alumina, are combined with only small quantities of silica, or, on the other hand, when large quantities of silica exist together with small

quantities of the above-named earthy bases. Silicates of alumina are difficultly fusible as long as they have not an opportunity of forming readily fusible double silicates with the silicates of lime, iron or manganese. In the presence of silica, the most injurious substances are the oxides of manganese, iron and alkalis, or any quantity of lead in the ores. The effect of these bodies in the process of reduction should be diminished as far as possible by the addition of zinc ores free from iron, manganese or lead. The ores classified according to these principles are then mixed with an excess of reducing agent. From the latter, lean (non-gaseous) coal is employed as free as possible from pyrites and shale, or else coal that has been carbonised—so-called "*cinder*"—or else small coke, or a mixture of raw and carbonised coals. At Freiberg lignite coke is also used as a reducing agent. An excess of the reducing agent is required both in order to bring the particles of ore into the most intimate contact possible with the carbon, and also to promote the formation of a certain quantity of carbon monoxide. The latter gas produces a certain tension in the vessels, which both prevents the passage through the pores of the walls of the vessels of the gases produced by the furnace fires, which, on account of the carbon dioxide and oxygen they contain, would have an oxidising effect upon the zinc vapours, and also expels these vapours into the condensers and prevents atmospheric air from passing into the latter. When coal is employed, hydrocarbons are evolved, which, in the case of heavy hydrocarbons, are dissociated at high temperatures, causing the separation of a certain amount of carbon, which is deposited in a finely divided state in the charge. This advantage is, however, counteracted by the fact that the expulsion of the gases from these coals requires heat, that the water vapour generated has an oxidising action upon the zinc, and that the zinc vapours are diluted by the expelled gases.

The quantity of the reducing agent has been increased at many works during recent years. For calamine and silicate of zinc, it amounts to from one-third to half of the weight of the ore, according to the zinc contents, and in the case of calcined zinc blende from half to two-thirds of the weight of the ore on account of its difficult reducibility. The grain of the ore and of the reducing material depends on the one hand upon the degree of reducibility of the ore, and on the other hand upon the form of the vessels in which the reduction is carried out. Silicate of zinc is more difficultly reducible than calamine or blende, and as it is only reducible by carbon, and not by carbon monoxide, requires to be brought into the closest possible contact with the reducing agent; both the ore and the re-

ducing agent must therefore be in the finest possible state of division, quite independently of the shape of the vessels of distillation. They should either be ground together or be mixed as thoroughly as possible after crushing. Zinc blende, which is more difficultly reducible than calamine, should also be ground to a very fine powder, say 0·04 to 0·08 inch mesh, as is indeed necessary for its calcination. It must be thoroughly mixed with the reducing agent, which should be crushed to about the same size. Calamine (calcined zinc carbonate) is reduced comparatively easily by carbon monoxide. It therefore requires no such intimate mixture with the reducing agent as does the silicate. If it has to be reduced in vessels of comparatively large capacity, such as muffles, it, together with the reducing agent, need only be crushed to bean or nut size. If it has to be reduced in tubular vessels which possess but a small capacity compared with the muffles, it must be crushed a great deal smaller, as also should the reducing agent. This is required with the object of filling thoroughly the tubes which are very strongly heated by the fire, as well as with the object of avoiding loss of zinc. This loss is partly due to the vessels remaining filled at the end of the process with zinc vapours which burn and are thus wasted when the residues are raked out; the more completely the vessel is filled, the less is the quantity of zinc vapour that can remain at the end of the distillation, on account of the proportionately larger quantity of residues that will be present.

The mixture of ore and reducing agent is either produced by simply mixing the above-named substances in a trough or upon the floor of the works, or else the ingredients of the charge, which have been first crushed separately, are ground together or mixed in pugmills. For instance, at Angleur, in Belgium, ore and coal are ground together in a Vapart mill down to 0·06 inch mesh. In order to prevent the ground mixture from being blown away during charging, and also to prevent its being blown out of the tubes by the pressure of the gases evolved in the latter, it is slightly moistened with water. The latter must, however, all be removed before the commencement of the distillation of zinc, otherwise the zinc vapours would be oxidised by it.

#### VESSELS IN WHICH THE PROCESS OF REDUCTION IS PERFORMED

The vessels in which reduction takes place are nowadays given the shape of either cylindrical or elliptical tubes known as retorts, or of prismatic boxes arched above, known as muffles; in England

crucibles used also to be employed. The various kinds of retorts, with their corresponding receivers, are shown in Figs. 71—73.

Fig. 71 represents one of the retorts of the Belgian furnace. The furnace itself contains many of these retorts arranged in rows one above the other. A muffle of the Rhenish-Westphalian furnace is shown in Fig. 72; each furnace contains two or three rows of these muffles.

Fig. 73 represents a muffle of the Silesian furnace. This furnace contains only one row of muffles, but the separate muffles are of much greater capacity than those of the other two just mentioned. These vessels must be made of the most fire-resisting materials pos-



FIG. 71.



FIG. 72.



FIG. 73.

sible. The zinc vapours escaping from them are collected in receivers attached to them, made of a less fireproof material, wherein these vapours can condense to fluid zinc. The gases which pass with the zinc vapours into the receivers or adapters, and which consist substantially of carbon monoxide, pass into an apparatus attached to the adapters in which any metallic portions carried off with them can be retained, whilst the gases are ultimately carried through flues or pipes into stacks. The material of which the vessels are composed is a mixture of fireclay and burnt clay, or burnt clay and quartz. In some works fragments of broken retorts, and in America coke, are also mixed with the fireclay. The great objection to these materials is that the clay is a bad conductor of heat, and will not stand great alternations of temperature; that it is attacked by the material of the charge, as also by high temperatures; that it is not quite close in

texture, but presents numerous minute fissures, and in consequence thereof allows zinc vapour to escape. Steger has therefore recommended the use of muffles made of magnesia bricks :<sup>1</sup> these have not, however, come into use up to the present. The mixture at present used consists of raw and burnt clay, or clean fragments of old vessels in place of the latter, and presents the greater resistance to fluxes, the higher the proportion of alumina as compared with that of silica. For this reason the attempts which have been made, for example in Upper Silesia, to add coarse-grained fragments of quartz to the mixture for making muffles has proved unsuccessful even in the case of basic charges. In Upper Silesia the vessels are made from clays obtained from Saarau, from Mirow, and more recently of clay from Briesen, near Lettowitz in Moravia, which is remarkable for its exceptional fireproof qualities. Clay from Striegau, mixed with sandy clay from Grojec or with kaolin from Saarau, Pentsch, Ruppersdorf, Göppersdorf, and with broken retorts and Neurode slate, is also used. The composition of these clays is as follows :—

Locality.	Saarau.		Briesen.					
Authority.	Steger. <sup>2</sup>		Steger. <sup>3</sup>					
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Silica . . . . .	49·00	50·41	44·76	44·88	45·46	44·64	44·87	45·61
Alumina . . . . .	36·75	32·66	39·25	39·93	39·00	39·60	39·76	39·31
Ferric oxide . . . .	0·80	3·23	0·48	0·99	0·01	0·01	1·14	1·13
Lime . . . . .	—	0·50	0·26	0·21	—	—	0·76	0·37
Magnesia . . . . .	0·56	—	0·36	0·08	trace	trace	trace	—
Potash . . . . .	0·41	1·56	1·55	0·52	—	trace	0·67	0·66
Soda . . . . .	0·37	—	—	—	—	trace	—	—
Loss on ignition . .	11·87	11·64	13·41	13·03	14·26	14·96	12·95	13·25
	99·76	100·00	100·07	99·75	98·73	99·21	100·15	100·33

In Nos. I. and II. 14 per cent. of the silica is in the form of sand. The clay, according to VII., contained 99·07 per cent. of pure clay, 0·32 per cent. of quartz, and 0·61 per cent. of felspar; that under VIII. contained 99·67 per cent. of pure clay and 0·33 per cent. of felspar.

The Briesen clay, which is in the form of hard lumps, is broken into grains about  $\frac{1}{2}$  inch in size and allowed to stand in a moist condition

<sup>1</sup> *Preuss. Minist. Zeitschrift*, 1894, p. 163.

<sup>2</sup> *Eisen und Metall*. 1888, p. 53.

<sup>3</sup> *Zeitschr. für das Berg-, Hütten- und Salinenwesen im Preuss. Staate*, 1896, p. 112.

for some months. It forms then an excellent material for the preparation of muffles.

Of the following analyses, I., II., and III. are of clay from Striegau,<sup>1</sup> a clay more readily affected by fire than that of Saarau. On heating, it shrinks strongly, as do the clays of Saarau and Briesen. Analysis IV.<sup>1</sup> is of Grojec clay, which is used in the crude form and is unshrinkable. As, however, it melts at a white heat, it can only be used in small quantities, mixed with other sorts. Analyses V., VI., VII., and VIII. are of Silesian kaolin,<sup>1</sup> which shrinks on heating until its chemically combined water is driven off, after which it expands owing to its high content of quartz. V. represents a kaolin from Pentsch, VI. from Ruppertsdorf by Strehlen, VII. a washed and burnt kaolin from Ruppertsdorf, and VIII. a kaolin from Göppersdorf dried at 100° C.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
SiO <sub>2</sub> . . . . .	68·00	53·86	58·02	65·39	57·59	61·60	54·70	49·42
Al <sub>2</sub> O <sub>3</sub> . . . . .	27·00	29·00	29·65	22·72	29·33	27·23	43·00	36·69
Fe <sub>2</sub> O <sub>3</sub> . . . . .	5·00	1·81	8·40	0·91	2·60	1·24	1·70	0·73
CaO . . . . .		0·46	1·15	—	0·74	0·38	0·30	0·09
MgO . . . . .		—	0·78	0·28	0·26	—	—	trace
K <sub>2</sub> O . . . . .		—	0·55	0·86	—	—	0·30	0·43
Na <sub>2</sub> O . . . . .		—	—	1·84	—	—	—	—
Loss on ignition . .	—	14·87	10·91	7·77	9·33	9·61	—	12·70

Steger (*op. cit.*) gives the following analyses of crude shale from Neurede (I.), the same shale burnt (II. and III.) (this forms the best diluent for the clay used in the preparation of muffles in Upper Silesia, as it is cheaper and more fireproof than fireclay), and a burnt shale from Rakonitz in Bohemia (IV. and V.).

	I.	II.	III.	IV.	V.
SiO <sub>2</sub> . . . . .	43·84	55·73	54·00	52·50	51·87
Al <sub>2</sub> O <sub>3</sub> . . . . .	38·30	42·69	44·92	45·21	46·39
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0·46	0·27	0·80	0·81	0·52
CaO . . . . .	0·19	0·28	0·48	—	—
MgO . . . . .	0·19	0·23	trace	0·54	0·45
K <sub>2</sub> O . . . . .	0·42	0·50	0·60	0·51	0·32
Na <sub>2</sub> O . . . . .	—	—	—	—	—
Loss on ignition . .	17·78	0·43	—	0·78	—

<sup>1</sup> Steger, *op. cit.* pp. 1-12.



The better qualities of fireclay used in Belgium for the manufacture of tubes have the following composition :—

Locality.	Andenne.	Namur.	Natoye.	Natoye.
Silica . . . . .	54	63	71	76
Alumina . . . . .	26	24	20	18
Ferric oxide . . . .	2	1	2	trace
Lime . . . . .	—	1	—	—
Water . . . . .	20	11	7	6

Further analyses are given in the next table (Steger, *op. cit.*).

	I.	II.	III.	IV.
SiO <sub>2</sub> . . . . .	49·64	57·95	73·58	71·79
Al <sub>2</sub> O <sub>3</sub> . . . . .	34·78	29·53	17·62	19·49
Fe <sub>2</sub> O <sub>3</sub> . . . . .	1·80	1·88	1·29	0·85
CaO . . . . .	0·68	1·72	1·24	—
MgO . . . . .	0·41	0·36	0·40	0·06
K <sub>2</sub> O . . . . .	0·41	—	—	} 0·85
Na <sub>2</sub> O . . . . .	—	—	—	
Loss on ignition . .	12·00	8·45	5·50	7·47

Here I., II., and III. are clays from Andenne, and IV. from Namur.

The following are analyses of certain varieties of clay used in the United States of America :—

Locality.	Wood-bridge. <sup>1</sup>	Wood-bridge. <sup>1</sup>	Cheltenham. <sup>1</sup>	Cheltenham. <sup>1</sup>	St. Louis, Mo. <sup>2</sup>	Perth Amboy, N.J. <sup>2</sup>
Silica . . . . .	42·85	42·83	50·19	50·16	50·80	46·90
Alumina . . . . .	37·32	37·01	30·08	30·47	31·53	35·90
Ferric oxide . . . .	1·18	1·04	2·79	2·48	1·92	1·10
Lime . . . . .	1·48	1·41	1·31	1·51	—	—
Magnesia . . . . .	0·41	0·46	0·47	0·29	—	—
Potash . . . . .	0·76	0·85	0·65	0·97	0·40	0·28
Soda . . . . .	—	—	—	—	—	0·16
Loss on ignition . .	16·36	16·27	14·65	14·62	13·80	14·30
Titanic acid . . . .	—	—	—	—	1·50	1·30

The St. Louis clay contained 12·70 per cent. of the silica as free quartz, and the Perth clay 6·40 per cent.

<sup>1</sup> *Berg- und Hüttenm. Jahrb. d. Akad.* vol. xxvii. Vienna, 1879.

<sup>2</sup> *Eng. and Min. Journ.* Nov. 25, 1893; *The Mineral Industry*, 1893, p. 650.

Analyses of various kinds of old broken retorts are here given :—

	I.	II.	III.	IV.	V.	VI.	VII.
SiO <sub>2</sub> . . . . .	41·13	50·10	50·20	48·64	46·50	52·14	49·75
Al <sub>2</sub> O <sub>3</sub> . . . . .	33·48	38·28	0·61	0·73	36·84	25·56	31·82
Fe <sub>2</sub> O <sub>3</sub> . . . . .	2·84	3·42	30·80	33·58	1·21	0·75	0·96
CaO . . . . .	0·92	1·13	0·48	0·35	0·60	0·40	0·52
MgO . . . . .	0·47	0·73	0·56	0·39	0·41	0·35	0·38
ZnO . . . . .	21·47	6·10	17·64	16·38	14·11	18·21	16·63
CdO . . . . .	—	—	0·005	0·07	0·08	0·01	0·13
MnO . . . . .	0·37	0·41	—	—	—	—	—
O + Na <sub>2</sub> O . . . . .	—	—	0·21	0·30	0·25	—	0·80

I. and II. are fragments of Belgian retorts, the former being the blue, the latter the white pieces;<sup>1</sup> III. and IV. are mixtures of ground fragments from the Kunigunden Works by Kattowitz and the Klara and Franz Works at Schwientochlowitz in Upper Silesia;<sup>2</sup> V. and VI. are the average analyses for the years 1885 to 1890 of retorts from the Beuthen and Rosamunde Works in Upper Silesia<sup>3</sup>; and VII. is the analysis of a sample of ground retort fragments from the Godulla Works in Upper Silesia.<sup>3</sup>

By the addition of quartz or sand the clay can be made richer in silica, and by the addition of a pure clay-slate, richer in alumina. With ores rich in quartz a certain amount, up to 10 per cent., of quartz may be added to the clay, but in the case of basic ores, it is advisable to employ clay as low in quartz as possible, or to add to clay rich in quartz certain qualities of clay or clay-slate very rich in alumina. As the charge is generally basic, it is in most cases preferable to employ in the manufacture of the vessels a material as rich as possible in alumina and as poor as possible in silica. In the preparation of the material, a portion of the clay is cleaned and dried; another portion is burnt. The burnt and dried clay, as well as the other materials which are to be added, amongst which may be clean fragments of old vessels, or coke, quartz, or sand, are ground, generally under edge rolls, and then moistened with water and mixed. The mixing is generally performed in pug mills or by shovelling and treading. The kneaded clay is allowed to lie for a time, usually from 4 to 6 weeks. The proportions of the various materials vary according to their quality. At the works in Upper Silesia the mixture averages 2 volumes of raw rich clay, 1 of raw

<sup>1</sup> Steger, *Eisen und Metall*. 1888, p. 66.

<sup>2</sup> Analyses by Jensch. See *Sammlung Chem. und Tech. Vorträge*, von Dr. Felx Ahrens, vol. iii. No. VI. p. 214.

<sup>3</sup> Jensch, *ibid.* p. 215.

sandy clay, and 5 of other materials. The rich clays are those of Briesen, Saarau, and Striegau, either singly or mixtures of two or three of these. The sandy clay is either that of Striegau, or the Silesian kaolin, or mixtures of both of these; and the other materials or diluents are powdered fragments of old retorts and burnt Neurode shale mixed in different proportions. The size of the grain of the clay is from  $\frac{1}{25}$  to  $\frac{3}{25}$  inch. The retort fragments and Neurode shale are ground under edge rolls and are in the form of dust, mixed with fragments up to  $\frac{2}{5}$  inch in diameter. The larger pieces increase the strength of the muffle and make it more able to stand change of temperatures and chemical erosion.

Great variety obtains in the proportions of the materials used at different works in Belgium, Westphalia, and the Rhine Provinces. In some works the mixture contains 40 parts (by measure) of unburnt, dark, rich Belgian clay, 50 parts of burnt, light, sandy Belgian clay, and 10 parts of coke. In other works the proportions of these three constituents are 36, 54, and 10 respectively; and elsewhere the proportions are 30 of rich, 10 of sandy Belgian clay, 50 of retort fragments, and 10 of coke. This last mixture is less fireproof than the preceding ones. Another composition used at Belgian works is 10 of raw Tahier clay, 10 of the same clay burnt, 8 of retort fragments, 1 of quartz, and 0.5 of coke.

Coke improves the fireproof qualities of clay and lessens shrinkage. In Belgium and in Westphalia near the Rhine the retorts are often glazed with aluminate and silicate of sodium in order to render their sides impervious to zinc vapour. In many works in Belgium, as also in Spain (Asturias Company, Province of Santander), considerable quantities of quartz or sand are added to clay rich in quartz, so that the vessels consist chiefly of silica. The latter is certainly less resistant towards fluxes than alumina; on the other hand, it stands fire well, is a good conductor of heat, and allows of thinner vessels being produced than does clay.

The receivers or adapters, which are used at present, receive the shape of cylindrical, conical, or bellied tubes, or of prismatic boxes arched on their upper sides, which are made of less fireproof material than the vessels used for distillation. In many places they are composed of equal parts of raw and burnt clay, or of ordinary clay, mixed with ground retort fragments and coke or coal ash.

To these adapters there are attached nozzles which may take the shape of cones or cylinders made of sheet iron, prismatic boxes made of clay, or prismatic boxes made of clay provided with a grating. These prismatic boxes are connected either with systems of tubes or

flues, through which the gases may be conducted into stacks, or with some other apparatus to collect the metallic particles that are still contained in them.

The shape of the furnace depends upon the shape and size of the vessels used for distillation. Those furnaces which contain vessels of circular or elliptical cross-section lying more or less horizontally are called Belgian Furnaces; those in which the tubes stand vertically are known as Carinthian Furnaces; those in which crucibles are used are known as English Furnaces; and those in which a single row of prismatic muffles arched on the upper side is employed are known as Silesian Furnaces. Furnaces containing many rows of small muffles are called Rhenish-Westphalian, or Belgo-Silesian Furnaces. The use of Carinthian and English furnaces has been completely discontinued, and they therefore now possess only an historical value. They will therefore only be considered here in general terms. The Belgian and Silesian furnaces, on the other hand, and the Belgo-Silesian furnaces, require detailed description.

The tubes or retorts of the Belgian furnaces are either circular in cross-section, with a diameter in the clear of 6 to 10 inches, and with a length of 3 feet 3 inches to 4 feet 9 inches, or, when the cross-section is elliptical, the long axis is  $8\frac{1}{2}$  inches in the clear, and the short axis  $6\frac{1}{4}$  inches to 7 inches; the walls are  $1\frac{1}{2}$  inches thick. The length is limited by the fact that the retorts are only supported at their extremities, and must therefore carry their own weight together with that of the charge without bending or breaking. They lie with one end on projections or ridges along the rear wall of the furnace, and with the other end supported upon ledges of clay in the front wall of the furnace and inclined towards the latter, as is shown in Figs. 74 and 75. This arrangement facilitates the removal from them of liquid matter and of residues.

Figs. 74 and 75 represent a Belgian furnace with flat grate: *c* are the retorts; *f* are the adapters; *g* the nozzles attached to the latter; *d* are the projections of the rear wall; *e* the clay slabs of the front wall upon which the retorts rest; *k* are plates of cast-iron which form the continuation of these clay slabs; *i* are bricks which support the adapters. The flames generated upon the grate *a* travel round the retorts, ascending in the shaft of the furnace, and escape at *l* out of the furnace proper and pass into the stack. The retorts are disposed in from 5 to 8 rows above each other, so that the greater portion thereof shall be surrounded by the flames. The furnaces are either single furnaces with only one shaft, or so-called double furnaces with two shafts separated by a vertical wall. The muffles of the

Silesian and Belgo-Silesian furnaces have the shape of prismatic boxes arched above, as is shown in the cross-section through the front end of a muffle in Fig. 76. The back side is permanently closed, whilst the front side is only closed during the process, the lower half by a clay tile, the upper half by the end of the adapter, or else by a tile which has an opening to receive the adapter. The adapter rests upon a step, which again is supported by projections in the muffle. A muffle with cylindrical adapter is shown in Fig. 77. More recently adapters of prismatic form have been used in Upper Silesia. The muffles do not exceed 26 inches in height—usually 24 inches—their width being from  $5\frac{1}{2}$  to  $6\frac{3}{4}$  inches; their length varies from 3 feet 3 inches to 7 feet. If the muffle is only supported at front and back, its length must not exceed 4 feet. A big Silesian muffle will take on the average a charge of 2 cwts. of calcined ore. The arrangement of a Silesian furnace fired by means of a grate and with descending flame, being the older type of the so-called Belgo-Silesian furnace, is shown in Figs. 78 to 82. Fig. 78 shows the longitudinal section on the horizontal line *CD*; Fig. 79 a sectional plan on the line *AB*; Fig. 80 a transverse section on the line *EF*. In

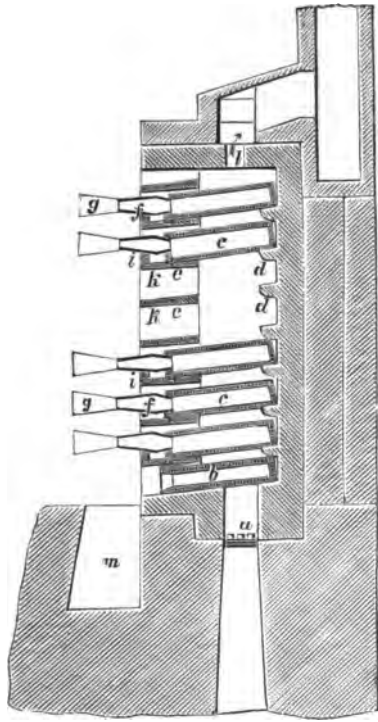


FIG. 74.

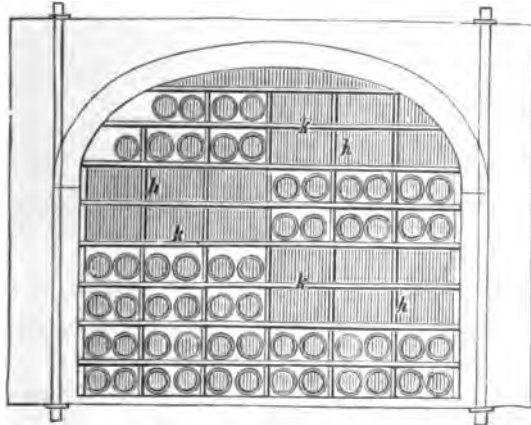


FIG. 75.

Fig. 78 shows the longitudinal section on the horizontal line *CD*; Fig. 79 a sectional plan on the line *AB*; Fig. 80 a transverse section on the line *EF*. In

these figures *c* are the muffles, of which 16 are disposed on either side of the grate; 2 furnaces, with 32 muffles in each, are combined together to form a block. The flame rising from the grate *R* surrounds the muffles *c*, and passes through apertures in the floor of the furnace into the flues *k*, which convey the products of combustion to the stack; *z* is a chamber for calcining calamine or for re-melting zinc; *v* are flues through which the residues from the

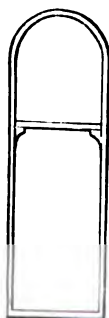


FIG. 76.

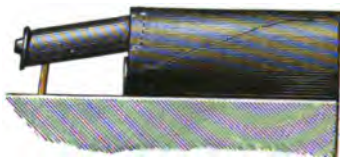


FIG. 77.

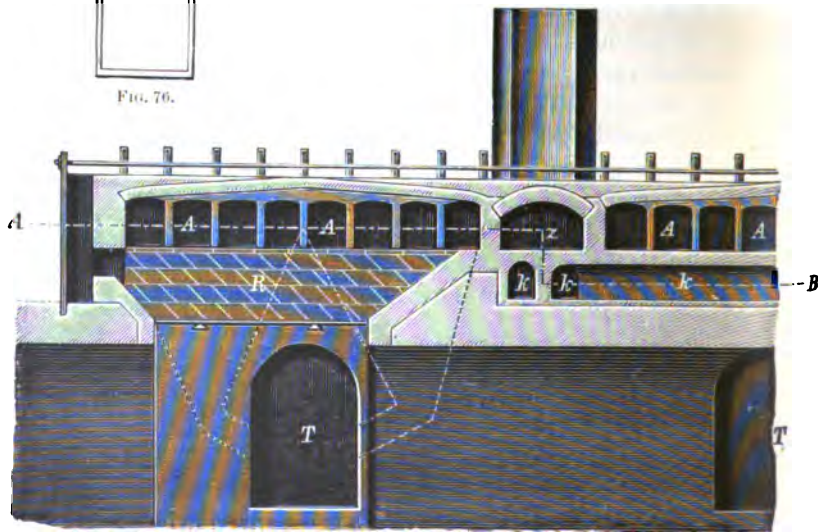


FIG. 78.

distillation, which remain in the muffles, are dropped into vaults *T*; these vaults open into a main vault *w*, which runs parallel to the longitudinal axis of the furnace; *u* are the adapters of the muffles, *q* the nozzles attached to these. The zinc collects in the swell of these adapters, and is raked out from them from time to time into an iron ladle held in front of the adapters, the nozzles being removed for this purpose. The adapters are placed in pairs in recesses into which the front ends of the respective muffles project for a length of

about 2 inches. These recesses, of which there are 8 on each longer side of the grate, are separated by partition walls *A*. The front of a pair of such muffles is shown on a somewhat larger scale in Fig. 81, in which *t* are the steps upon which the back-end of the adapter is supported. The front-end rests upon an iron frame, which is also represented in Fig. 82 upon a somewhat larger scale. The latter

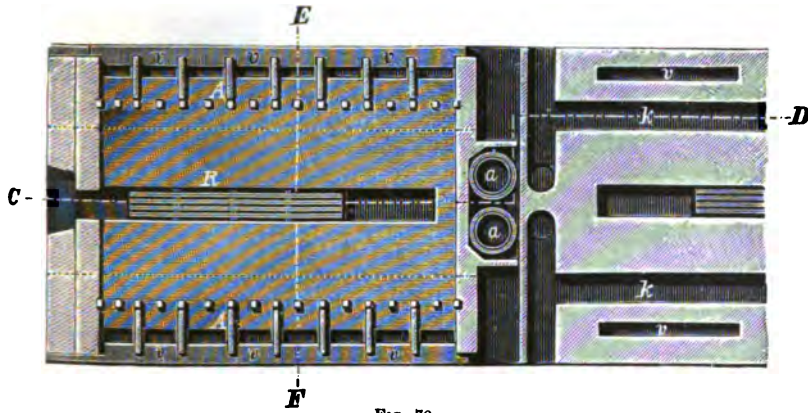


FIG. 79.



FIG. 80.

closes the recesses in front, and is completely closed below by means of a door *y*.

At some works several rows (up to 3) of muffles are placed one above the other. Such a furnace fired by gas and containing 3 rows of muffles, holding altogether 50 to 55 muffles, which is in use in the Rhine Provinces, is shown in Fig. 83: *m* are the muffles; the two upper rows rest upon benches formed of strongly fireproof clay;

*v* are the adapters for the collection of the zinc. The producer gas, generated in a producer not shown in the drawing, passes through the flue *a* into the vertical flue *b*, and is there mixed with the air for combustion, which enters the flue *c* through the flues *l*, and passes thence through *d* into *b*. The flame rises up to the arch of the

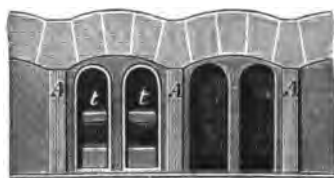


FIG. 81.



FIG. 82.

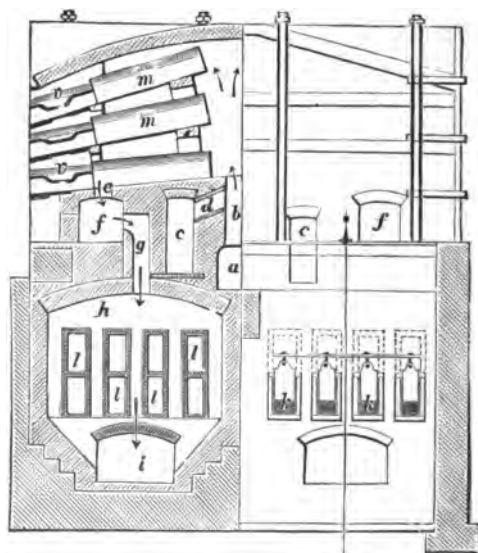
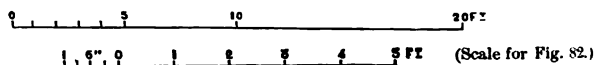


FIG. 83.

heating chamber, then returns and descends through the openings *c* into the flue *f*, whence it passes through flues *g*, *h* and *i* into the stack. On its passage through the flue *h* it surrounds the air flues *l*, by means of which the air used for combustion is heated.

In England<sup>1</sup> the vessels for distillation used formerly to be large crucibles composed of a mixture of 7 parts of best Stourbridge clay.

<sup>1</sup> Percy, *Metallurgy*, p. 555.



5 parts of a second-quality clay, 3 parts fragments of glass pots, and 6 parts of fragments of old zinc crucibles. These crucibles were notable for their exceptional durability. Each of them could contain 368 pounds of calcined zinc blende. The crucibles were heated in a furnace arranged like a glass-melting furnace. The zinc vapours, evolved during the process of distillation, escaped through an opening in the bottom of the crucible into a vertical descending pipe. In the latter they condensed and trickled into a vessel of sheet-iron placed at the bottom. The distillation was accordingly a distillation *per descensum*. The construction of such a crucible with its tube attached is shown in Fig. 84. The crucible was charged through the opening on top, the removable cover being taken away for this purpose. These openings were accessible through openings in the vault of the furnace, also provided with covers. The tube for conducting away the zinc vapours was composed of sheet-iron, and was made in two parts, *b* and *c*. The upper portion *b* was held in an iron ring which rested upon a cross piece *d*, welded to the perpendicular iron rods *f*,

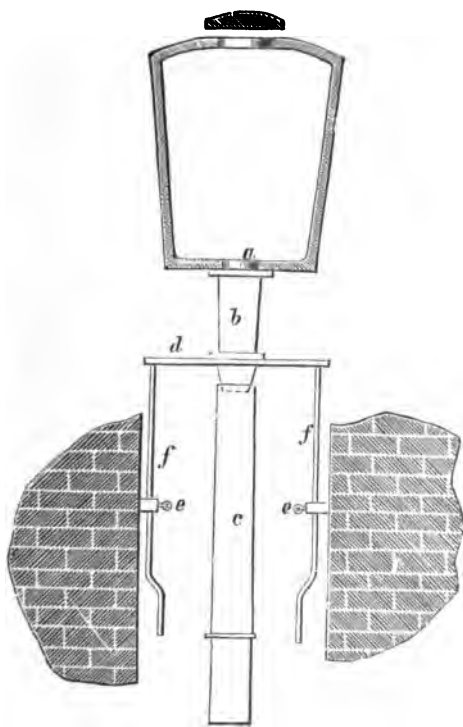


FIG. 84.

which pass through eyes secured to the furnace. The iron rods could be raised or lowered in these eyes and clamped in any desired position. By pushing the rods up, the upper portion of the tube, which was provided with a flange, could be brought into close contact with the bottom of the crucible. The lower tube was pushed into the upper one and fastened by being turned round in it. Below the bottom tube there was an iron vessel to collect the zinc. The construction of the English furnace is shown in Fig. 85, in which *c* are the crucibles, 6 in number, which were placed on either side of

the grate *a*. The flames, after heating the crucibles, passed through openings *g* in the vault of the furnace into the flue; *b* is the fire-door. The crucibles were inserted in the furnace through arched openings *m*, which were closed during the operation by means of movable walls built of brick lumps. In the latter there were small openings *c*, which could be more or less closed as required by means of bricks, the fire-door being kept closed by means of a shovelful of coals. The openings *c* served to clay up any cracks in the crucible

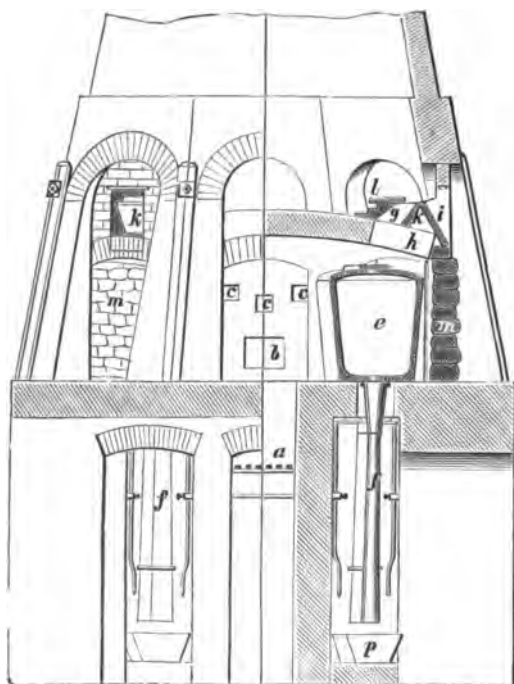


FIG. 85.

that might form in the side exposed to the fire. The crucibles were charged through the openings *h*, which were kept closed during the operation by means of a tile *i*. The gases escaped through the aperture *g* into the flue, a tile *l* being used for regulating the draft: *f* is the tube through which the zinc vapours were conducted down; *p* the sheet-iron vessel in which the condensed zinc was collected. The residues after distillation were removed through the opening in the bottom of the crucible. These

English furnaces have been entirely disused, and have been replaced by Belgian or Silesian furnaces on account of their high consumption of fuel, 1 ton of zinc requiring from 22 to 27 tons of coals.

Vertical retorts have not so far come into definite use. They labour under the disadvantage that the charge gets packed so tightly as to hinder the passage of the zinc vapour through it.

At Delach, near Greifenburg, in Carinthia, small vertical tubes were used at the commencement of last century in the process of distillation.<sup>1</sup> These tubes were closed at their upper wider end.

<sup>1</sup> Hollunder, *Tagebuch einer Met. Reise*, Nürnberg, 1824, p. 273; Percy, p. 585.

and opened at their bottom end into a tubular receiver through which the zinc vapours passed into a chamber common to all the tubes in which the vapours were condensed. The floor of this common receiver was formed by an iron plate upon which the zinc trickled down. Eighty-four such tubes were placed in a reverberatory furnace. The tubes were 3 feet 3 inches long,  $4\frac{1}{2}$  inches in diameter at the top, and  $3\frac{1}{4}$  inches at the bottom. Only from 5 to 7 lb. of ore were charged into each, the upper empty portion of the tube, 4 inches long, being filled with small pieces of charcoal. This method of distillation has long been abandoned on account of the high costs connected with it. Recently vertical tubes of larger diameter for the treatment of lead-bearing zinc ores have been proposed by

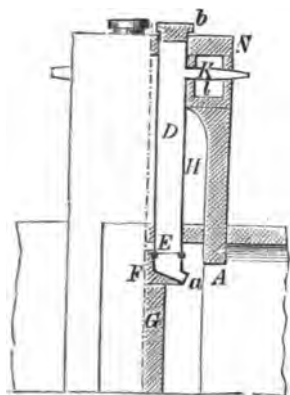


FIG. 86.

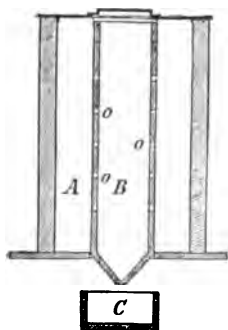


FIG. 87.

Chenhall,<sup>1</sup> by Binon and Grandfils,<sup>2</sup> by Keil,<sup>3</sup> P. Choate,<sup>4</sup> and by Grützner and Köhler.<sup>5</sup> The furnace of Binon and Grandfils, which possesses such tubes arranged for continuous working, with adapters to collect the zinc at their upper ends, and with an opening at the lower end for the removal of the residues of distillation and for the collection or tapping off of the lead, is shown in Fig. 86. *D* is the tube, 8 feet 10 inches long and  $15\frac{1}{4}$  inches in diameter. It stands in a cast-iron tube *E* filled with clay, which is attached to the upper portion of a boot-shaped projection *F*. The upper opening of the tube, through which it is charged, is closed by means of a cover *b*. *K* is a conical adapter for the collection of the zinc vapours. Each

<sup>1</sup> *Oesterr. Zeitschr.* 1880, p. 462.

<sup>2</sup> *Ibid.* 1881, p. 325; *Dingl. Polyt. Journ.* vol. 235, p. 222.

<sup>3</sup> *Berg- und Hüttenm. Ztg.* 1888, p. 116.

<sup>4</sup> *Eng. Pat.* 530, 1893; *Amer. Pat.* 489460.

<sup>5</sup> *D. R.-P. No.* 58026, September 25, 1889.

furnace contains 12 to 16 of such tubes, which stand upon the cast-iron boxes *F*, which in their turn are supported by the brick pillars *G*. The tubes are heated by gas, which is burnt in the flues *H* by the aid of air previously heated.

The furnace of Grützner and Koehler is arranged similarly to that of Binon and Grandfils. The zinc vapour is led off through a hole in the cover of the retort (not in the side), and another hole in the cover serves for charging. Several such retorts are arranged radially to the axis of the furnace, and the hot gases pass up the central part of the furnace, whence they envelop the separate retorts.

Choate condenses the zinc vapour in the cylinder *B* inside the retort *A* (Fig. 87). The vapours pass through the holes *O*, and the

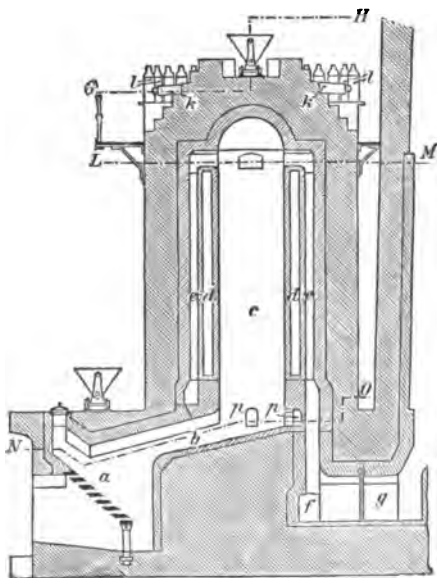


FIG. 88.

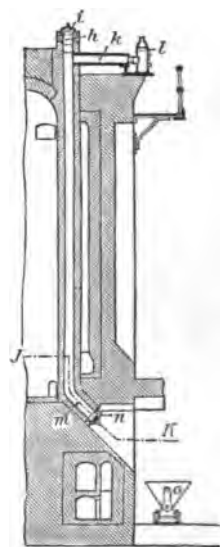


FIG. 89.

liquid zinc runs away at the lower conical end of the condenser, into the vessel *C*. Retorts fired only from outside would probably not allow the charge to get sufficiently heated. Nothing is known to the author as to their application on a large scale, and the practical results obtained in these tubes.

The furnace proposed recently by Carl Francisci<sup>1</sup> possesses a vertical annular retort which is heated inside and out by producer gas. It is charged from the top, and the residues are drawn at the lower end from a series of discharging openings. The receiver is

<sup>1</sup> German Patent, 107247.

fixed at the top end of the retort. The arrangement of this furnace is shown in Figs. 88 to 95.<sup>1</sup> The ring-shaped retort is shown at *d*, the producer at *a*, and the air-flues heated by waste gas at *p*. The burning gases rise through the internal shaft *c*, and are drawn

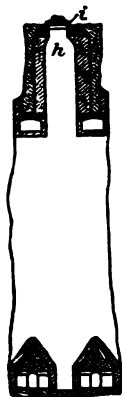


FIG. 90.

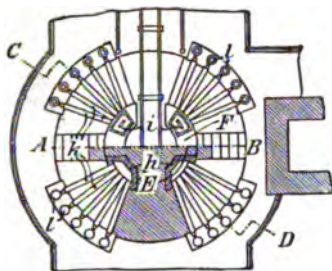


FIG. 91.

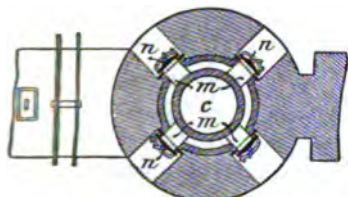


FIG. 92.

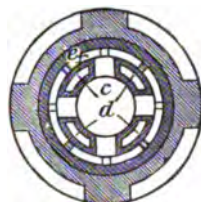


FIG. 93.

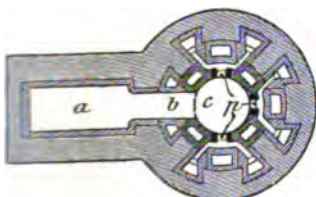


FIG. 94.

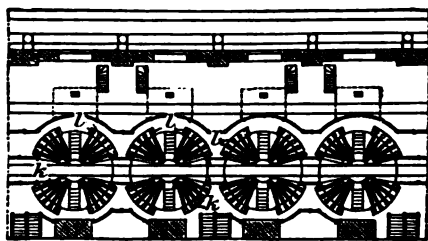


FIG. 95.

down the channel *e* around the outside of the retort; thence they pass into the flue *f* into the flue *g* leading to the stack. The material is charged through the openings *h*, which are closed by the lid *i* during the distillation. The zinc vapour passes into the

<sup>1</sup> Steger, *Preuss. Zeitschr. für Berg-, Hütten-, und Salinenwesen*, 1900, pp. 404, 405.

receivers *k* at the top of the retort, and these are connected with the chambers *l*. The discharge is through the shoots *m*, which are closed during distillation by the covers *n*. Fig. 95 represents a block of four of these furnaces. Magnesia bricks may be used with this type of furnace. The retorts should be anchored in the case of furnaces built of separate bricks.

#### GENERAL CONSIDERATIONS RESPECTING THE PROCESS OF REDUCTION

As will be seen from the above statements, the process of reduction is carried on in comparatively small vessels more or less readily destroyed, which do not admit of continuous action, and are expensive to produce, whilst the cost of fuel and wages is high. If to this is added that the extraction of zinc is an imperfect one, ranging from 70 to 90 per cent. of the zinc contents of the ore, because the losses of zinc amount, under the most favourable circumstances with rich ores, to 10 per cent. of the contents of the ore, and in the case of poorer ores to 30 per cent., being due to zinc remaining behind in the residues, to zinc vapours that remain in the vessels at the end of the distillation, and the burning of the latter when the residues are removed, to imperfect condensation of zinc vapours, to the escape of zinc vapours from the vessels, and to the retention of zinc as an aluminate in the walls of the vessels, the present process of zinc extraction must be considered as a highly imperfect one, when compared with the processes for the extraction of metals which are not volatile when reduced in the dry way. In consequence of the above-named difficulties, poor zinc ores cannot be utilised at all for the extraction of zinc. It is therefore intelligible that metallurgists have long been striving to replace the present discontinuous process by a continuous process in shaft furnaces. The whole of the attempts in this direction have, however, as far as regards the extraction of metallic zinc, given unfavourable results. Having regard to the difficulty of the condensation of zinc in vapours which are diluted to a high degree by the products of combustion and by the nitrogen of atmospheric air, such as is the case with zinc vapours obtained from shaft furnaces, it is not probable that the problem of the direct extraction of zinc in such furnaces will be satisfactorily solved. It is, however, highly probable that ores poor in zinc may be worked in shaft or reverberatory furnaces and yield intermediate products rich in zinc, as for instance, mixtures of pulverulent zinc with small quantities of oxide, or zinc oxide, which would form a suitable material for zinc distillation in appropriate vessels.

Having regard to the small probability of success in the direct zinc extraction in shaft or reverberatory furnaces, efforts during the last 20 years have been directed to the improvement of the process of zinc extraction in its actual form, with favourable results. These improvements consist chiefly in the introduction of gas-firing, the utilisation of natural gas, as at Kansas, Indiana, in increasing the size of the furnaces, in improving the fireproof qualities of the material employed for the vessels, and in the production of these with dense walls by the employment of hydraulic pressure, the improvement of the apparatus used for the condensation of zinc vapours, and for the removal of condensed zinc from the adapters, for the collection of the zinc which has not been condensed in these, and for keeping the interior of the zinc works free from fumes. We have therefore to consider as the only method of zinc extraction used up to the present in the dry way, the distillation of zinc in vessels and its chief variations:—

- (1) Distillation in horizontal retorts, or the Belgian method.
- (2) Distillation in muffles, or the Silesian method.
- (3) Distillation in Belgo-Silesian furnaces.

The other above-named methods, viz., the English and the Carinthian, are no longer in existence, and need therefore no further consideration.

#### COMPARISON OF THE PROCESS OF DISTILLATION IN RETORTS AND MUFFLES

The differences between distillation in retorts and in muffles have been pretty well equalised since the introduction of gas-firing. There are districts in which distillation is carried on in retorts to as much advantage as it is in muffles, as for instance the Rhine Provinces, Westphalia, and Belgium. As long as ordinary grates only were used for zinc distillation, the choice between retorts and muffles depended generally upon the flame-giving quality of the coals. Distillation in retorts required coals giving a long flame, whereas distillation in muffles could be performed also with coals that gave but a short flame. Only in recent times has it been rendered possible by means of special construction of grates to use fuel giving a short flame also for the heating of retorts. For example, in the United States by burning anthracite coal upon what are known as Wetherill grates, consisting of cast-iron plates with conical holes, by means of heated air, a long flame suitable for the heating of retorts has been obtained. Hence it happens that in districts which yielded coals giving short

flames, as in Upper Silesia, muffles were first employed, whereas in districts in which fat or long-flaming coals were available, as in the Rhine Provinces, Westphalia, and Belgium, both retorts and muffles came into use. By the introduction of gas-firing in its various modifications, and of the above-mentioned Wetherill grates, the choice of the vessels employed has been rendered independent of the flaming properties of the fuel.

Belgian and Belgo-Silesian furnaces are generally used at present, the former being preferred in the case of ores (like siliceous calamine) hard to reduce, while the latter are best suited to all other kinds of ores. These two classes of furnaces are used in Belgium; in the Rhine Provinces and Westphalia the Belgo-Silesian furnace is employed. Silesian furnaces are used in Silesia for the treatment of coarse-grained material containing both calamine and blende. At many works, owing to the shortage of calamine and the need of increasing the quantity of blende in the charge, it is now necessary to have resort to the Belgo-Silesian furnaces. These are better adapted for smelting compact, fine-grained charges of blende than the high and capacious Upper Silesian muffles. With the exhaustion of the calamine supplies, and the necessity for treating blende alone, use will have to be made of the smaller and shorter thin-walled muffles and furnaces of the Belgo-Silesian type. Belgian furnaces, and, only exceptionally, Silesian furnaces, are used in England. In Spain and the United States, Belgian furnaces are used. In general, Belgian furnaces are used for ores difficult to reduce, and both Belgian and Belgo-Silesian furnaces for ores of high and middling zinc-content. Silesian furnaces are only exceptionally employed in the case of coarse ores with low zinc-content containing calamine.

The question how poor an ore may be and still be treated profitably depends, apart from the price of zinc, upon the rate of wages, the cost of fuel, and the cost of fire-resisting materials. The item of coal is the highest, next comes that of wages, and lastly that of fire-resisting materials. For example, the costs of distillation per ton of calcined ore in Belgo-Silesian furnaces, under conditions obtaining in the Middle Rhine Provinces, are distributed as follows, according to Lynen<sup>1</sup>:—

Coals . . . . .	15s.
Wages . . . . .	12s.
Fire-resisting materials . . . . .	6s.
Maintenance and general expenses . . . . .	7s.

<sup>1</sup> *Zinc distillation furnace with common condensing chamber, London, 1893.*



In Rhenish Westphalia ores (blendes) are treated containing at least 40 per cent. of zinc; under particular conditions calamine with 20 to 30 per cent. of zinc can be worked along with the blende. In Upper Silesia grades of calamine with only 8 to 9 per cent. of zinc can be treated along with blende containing at least 30 per cent. of zinc.

As the outlay for coals forms the chief item in the cost of zinc extraction, zinc works should as a rule be erected in the neighbourhood of coal-mines, and the ores should be carried to the coals, not the coals to the ores. For 1 part by weight of zinc 4 to 10 parts by weight of coal are consumed.

### I. THE BELGIAN METHOD OF ZINC DISTILLATION

As already stated, this method of distillation is performed in retorts lying at a flat angle of inclination and heated in externally-fired shaft furnaces. The zinc vapours thus formed are condensed in conical adapters provided with nozzles.

*The tubes or retorts* are made of the following shapes and dimensions. Those of circular section are 6 to 10 inches in diameter and 39 to 50 inches long in the clear, and the sides are  $\frac{1}{4}$  to  $1\frac{1}{2}$  inches thick. The capacity of the tubes at Vieille Montagne is  $1\frac{1}{2}$  to  $2\frac{1}{2}$  cubic feet. Those of elliptical section are 8 to 9 inches along the major axis and 6 to 7 inches along the minor; their length in the clear is 4 feet 9 inches, and the thickness of the sides is  $\frac{1}{4}$  to  $1\frac{1}{2}$  inches. Quite recently the walls have been made only  $\frac{3}{4}$  inch thick, the material consisting chiefly of silica similar to Dinas brick. At La Salle, Illinois, U.S.A., retorts have been used rectangular in cross section and of large dimensions, which have to resist the first attack of the flames, the firing being by gas; their outside dimensions are 5 feet long, 20 inches high, and 9 inches wide.

The material of which the retort is made has already been referred to. Recently material containing 94 per cent. of silica and but little alumina has been used, especially in Belgium and Spain, in the case of ores containing much quartz. Such siliceous tubes cost less and can be made thinner-walled ( $\frac{3}{4}$  inch) than those made from clay, and they have the further advantages that the heat passes rapidly through the walls, and the material of the tubes is but little corroded by siliceous ores. The mixtures employed at the different works vary greatly and depend upon the contents in quartz and alumina of the various materials that are obtainable, as also upon the nature of the gangue of the ores. In many works finely ground

coke is added to the materials employed in order to make the retorts firm, smooth, and impenetrable to zinc vapours. Retorts made from material rich in quartz are glazed for the same purpose with a glaze consisting of 60 parts of loam, 30 parts of glass, and 10 parts of soda. The other class of retorts is often glazed externally with aluminate and silicate of soda. If the mixture contains too great a quantity of raw clay, it becomes less fire-resisting; if it contains too much burnt clay, it is difficult to mould, and the tubes become porous and brittle. For example, the mixture used for retorts at the Engis Works, in Belgium, for a long time consisted of 30 parts of raw clay, 27 parts of burnt clay, 15 parts of old retorts, 18 parts of coke, and 10 parts of sand. Another mixture used in Belgium for retorts made by machinery<sup>1</sup> is as follows:—

	Parts by Volume.
Coke . . . . .	100
Sand . . . . .	300
Old Retorts . . . . .	250
Raw Clay . . . . .	350

In England, at Morriston, the mixture for the lower, air-cooled retorts, consists of 1 volume of raw Belgian clay from Andenne: 2 parts of burnt Belgian clay, 1 part of raw and 1 part of burnt Stourbridge clay, all by volume, or else 1 part by volume each of raw and burnt Belgian clay, raw English clay, fragments of old retorts, and Belgian sand. For ordinary retorts, the mixture is 1 part by volume of Belgian clay, 1 part of English clay, 3 parts of old retorts or 1 part of Belgian clay, 1 of English clay, 1 of burnt Belgian clay, 1 part of old retorts, and 1 part of old fire-bricks. In the United States of North America equal parts of fresh and burnt clay are used. The latter may consist either of clay freshly burnt or of the fragments of old retorts. A mixture of quartzose material which has been quite recently employed has the following composition: one-third clay from Andenne with 60 to 70 per cent. of silica, one-third sharp-edged sand, and one-third burnt clay. The mixture contains 94 per cent. of silica.

The above materials are first crushed, then kneaded together to a uniform mass, with the addition of 7 to 8 per cent. of water. Crushing is performed by means of edge runners, Carr's disintegrators or Vapart's disintegrators. The latter apparatus, generally used in Belgium, will grind from 3 to 3½ tons per hour. If the grain is too coarse, the retorts will be porous: if, on the other hand, it is too fine.

<sup>1</sup> Knab, *Metallurgie*, p. 431.

the retorts readily soften in the fire. The clay is ground to a fine flour, whilst burnt clay and fragments of retorts are passed through a sieve of 0·2 inch mesh, but the average grain of the whole does not, as a rule, exceed 0·12 inch. The materials are kneaded together in an ordinary pug mill, and only exceptionally by hand. After kneading, the mass is usually allowed to lie from 6 to 8 weeks in cellars to make it more plastic; it is then cut up into lumps. The manufacture of retorts may be performed by hand or by machine, machines being mostly employed, hand work having been given up at present at most works. Retorts when made by hand are mostly made by means of sheet-iron moulds, which consist of several sections; each section consists of halves, each of which has the shape of a hollow semi-cylinder. The two faces are then placed together, when they form a cylinder, and are kept together by means of rings and wedges. Into the bottom part of the mould a disc of clay is placed, which is then hollowed by means of a stamper to form the bottom of the retort, so that the edges of the disc rise up to form the commencement of the walls of the cylinder. The portion of the disc that has been forced up is now beaten against the wall of the mould by means of a beater, and then scraped and smoothed out by the help of a sweep. The upper edge of that portion of the retort that is thus produced is then scored with a comb-shaped board, when it can be lengthened to the required extent by the addition of rings of clay. As soon as these rings have reached a certain height, the cylinder thus formed is surrounded by a new segment of the mould. The clay is once again beaten against the wall of the segment that has been put on, and is again bored out by the help of the sweep. The upper edge of the tube thus prolonged is again scored, and the previous process is repeated, and continued until the retort has reached the desired height. A small ring of clay is then placed upon the top edge and pressed inwards in order to strengthen the wall of the retort at this point. Finally the upper edge of the retort is cut smooth. It, together with the inside of the retort, is planished, and the whole is then placed in a well-ventilated room. A workman can produce from 18 to 20 retorts in 12 hours. After some 48 hours the various segments of the mould are removed gradually, and the retort is then allowed to stand for another three weeks until it is completely air-dried. It is then dried for two or three months in chambers heated by furnaces or stoves to a temperature of 25° C. at first, rising ultimately to 70° C. The longer the retorts are allowed to remain in these heated drying chambers, the better do they stand in use. Another, but less common, method of manufacturing retorts by hand consists

in placing a cylindrical core into the mould and ramming the material of which the retort is to consist into the ring-shaped space left between the mould and the core.

The manufacture of retorts by machinery is performed in various ways. The older method, which is still in use in isolated cases, consists in forcing the clay wrapped in linen into a vertical, cylindrical or elliptical wooden mould arranged to open, and then boring out, by means of a drilling machine, a cylindrical or elliptical hole in it. The clay is forced in by means of a hammer moving up and down. After the mould has been filled in this way it is carried with its contents to the boring machine, which then hollows it out. The mould is then opened, and the retort is taken out and carried into the drying chamber, where its linen covering is removed and the inside smoothed. At Angleur three men and two boys can make 140 retorts in this way in 10 hours.

A second method, which is now used at most of the Belgian zinc-works, consists in first moulding the clay into the form of solid cylinders, and then pressing these into the shape of retorts by hydraulic machinery. By these means the bottom of the retort is made in one piece with the tube. The solid cylinders are 1 foot 8 inches in diameter, and 2 feet in length. They are produced by pressing lumps of clay into cylindrical or elliptical moulds, the bottom of which is formed by a hydraulic piston. After the clay has been rammed sufficiently firmly into the mould with hammers, it is forced out of the mould by means of a hydraulic ram, and then, by means of hydraulic presses, forced into the shape of the retort. There are various forms of these hydraulic retort machines in use. One of them consists of a vertical cylinder of cast steel, the interior of which has the shape and dimensions of the exterior of the retort. Inside it there is a hollow core of the shape and size of the interior of the retort to be moulded. A lump of clay is first thrown into the cylinder to form the bottom of the retort. The upper end of the cylinder is then closed, and by means of a hydraulic ram a pressure of from 150 to 200 atmospheres is exerted upon the clay in the cylinder, from beneath. The bottom is formed by pressing the clay against the cover of the cylinder, the walls by the clay being forced into the annular space between the cylinder and the core; the pressure is kept on for some 2 minutes. After this, the cover of the cylinder is taken off, and the retort is forced out of the mould by allowing the hydraulic cylinder to rise. When it has reached the desired length, the retort is cut off by means of a wire.

To this class belongs the moulding machine of N. J. Dorr in

Ampsin,<sup>1</sup> a vertical section of which is shown in Fig. 96. The cylinder, which can be worked under a pressure of 200 to 300 atmospheres, is shown at *a*, and the piston at *b*; the latter can also work in the cylinder *e*, which holds the clay. *o* is the retort cylinder and *i* the core, the top of which, *J*, corresponds in section to the inside of the retort, and is perforated at *k* with a hole which allows of the passage of air into the retort. The mould *l* at the end of the cylinder gives the retort its external shape, and *g* is the cylinder cover, which can be removed by pressing the rod *s*. After the cylinder *e* has been filled with clay the piston presses the clay into the retort cylinder *o*, where the retort is formed. The cylinder *e* is fixed to four columns *n* by means of four cast stay-pieces, and is forced against the collar *f* during the compression of the clay by the two hydraulic presses *c*. When the compression is over, the piston is allowed to fall, and the cylinder *e* sinks into *a* and is again filled with clay. The core *i* is carried by an arm cast into the collar *f*, and the latter is bolted on to the bearer *m*.

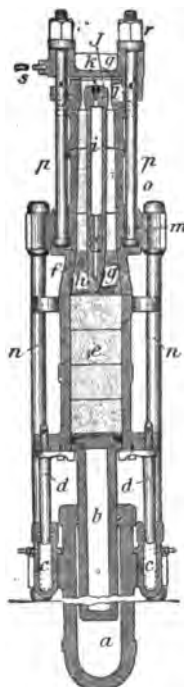


FIG. 96.

Another form of moulding machine consists of a vertical hollow cylinder of cast steel, in which there is an annular piston which fits exactly into the interior thereof. Inside the annular piston there is a cylindrical core of the shape of the interior of the retort; both pistons work from below upwards. The top of the cylinder is closed by a heavy cover of cast steel. To make a retort, a cylindrical block of clay of the requisite size is introduced into the cylinder, the top of which is closed. Both pistons are at first pressed simultaneously upwards to compress the clay; thereupon the inner cylinder or core is forced into the clay, whilst the annular cylinder sinks back. By this movement the retort receives the shape required. After it has been formed, the upper end of the cylinder is opened, and by forcing up the annular cylinder the retort is pressed out of the apparatus; here also the pressure amounts to 150 to 200 atmospheres, and is applied for some 2 minutes. A machine of the first kind is used, for example, at Ampsin in Belgium. This machine will make 145 retorts in 10 hours, with the labour of 4 men per shift. Another man is required for moulding the clay cylinders, and another removes

<sup>1</sup> Steger, *Preuss. Zeitschr.* p. 418,

the finished retorts into the drying-house. A machine of the second class is in use at the Munsterbusch Works, near Stolberg, for the manufacture of muffles; 140 to 150 muffles are there produced in 10 hours, three men being required. Retorts manufactured by the aid of hydraulic machinery are better and more durable than those produced by hand, chiefly because the walls are denser, so that the loss of zinc has become considerably less since they have come into use. Retorts made by machinery are dried in the same way as those made by hand. Before the retorts are introduced into a furnace in operation, they must be heated for a time in a kiln to prevent their cracking and bending. They must be heated up to a red heat for 12 to 24 hours, and must be turned round at half time.

The kilns in which the retorts are heated before being used are reverberatory furnaces, through the beds of which pass numerous perforations. The retorts are placed in the heating chamber above this bed. The grate is either below the perforated bed, so that the flames

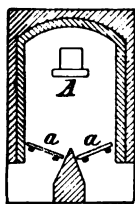


FIG. 97.

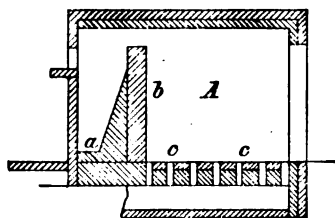


FIG. 98.

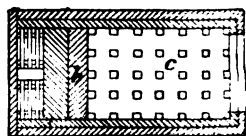


FIG. 99.

pass through the openings in the latter from below upwards, or else it is on one side, and the flame passes over a fire-bridge into the upper part of the heating chamber, passing through the latter from above downwards, and escaping through the openings in the hearth into the flues. A furnace of the latter kind, which is said to have done exceedingly good work, and to have been very durable, and which is preferred in England to kilns of the first kind, is shown in Figs. 97 to 99. *A* is the heating chamber, 7 feet long, 4 feet 6 inches wide, and 5 feet high in the centre, holding some 25 retorts; *a* is the fire-place; the grate, 4 feet 3 inches long and 12 inches wide, consists of halves inclined towards each other; *b* is the fire-bridge over which the flame passes into the heating chamber. The flame traverses the latter from above downwards, and passes through the apertures *c*, 4 inches square, in the bed, into the flue which leads the products of combustion into the stack.

*Adapters*

The adapters, in which the gaseous zinc condenses, are short conical tubes of clay, which is, however, less fire-resisting than the clay of the retorts. They are usually composed of a mixture of equal parts of raw and burnt clay. In England the mixture consists of one part of clay from Andenne, one part of Stourbridge clay, and four parts of old retorts and bricks. The mixture is either formed into sheets and turned round cores and then beaten firmly against the latter, or else it is pressed into a conical metal mould, into which a core is forced. The piece thus made is carefully dried, smoothed inside, and finally burned. These adapters are about 16 inches long, 6 inches in external diameter at the wide end, and 3 inches at the narrow end. A workman can make 100 of these in

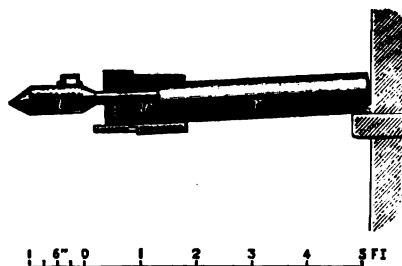


FIG. 100.

a day. Before being used, they are coated with milk of lime, so as to enable any accretions that may form in them to be removed without difficulty. The wide end of the adapter fits into the retort, the space between the two being filled up with clay. An adapter lasts from 8 to 10 days. The fragments of old adapters after being cleaned can be used for the manufacture of firebricks of inferior quality. The mode of attaching the adapter and its position with respect to the retort are seen in Fig. 100, the wide end of the adapter being luted to the retort *r*; the front narrow end rests upon a brick. To it is attached the so-called nozzle *v*, which is made of sheet-iron, and serves to catch any particles of metal that may be carried off by the vapours; it is secured by means of wires, which are made fast to the front wall of the furnace. Carbon monoxide generated in the retorts burns on leaving the nozzle.

Other forms of nozzles are seen in Figs. 101 and 102.<sup>1</sup> In Fig. 101,

<sup>1</sup> Steger, *Sammlung chem. und chemisch-technischer Vorträge*, Ahrens, vol. i. No. 2, p. 61.

$s$  is the peep-hole at which the gases are evolved. The nozzle depicted in Fig. 102 is supplied with partitions  $z$  in order to promote the precipitation of the zinc dust. The gas burns at  $i$ . Instead of nozzles, a system of pipe-chambers may be used with advantage, as

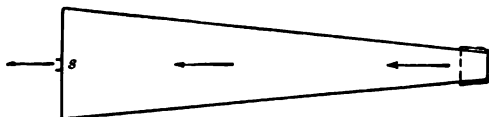


FIG. 101.

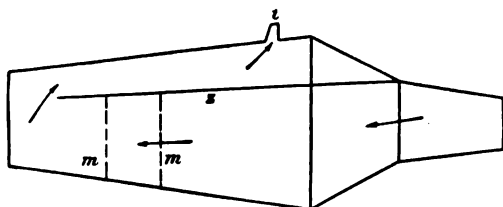


FIG. 102.

shown in Fig. 103. (Steger, *ibid.*)  $U$  is the lower chamber with peep-hole, into which is fastened at  $o$  the upper chamber consisting of the arms  $a_1$ ,  $a_2$  and  $a_3$ .  $ss$  are sheets of iron attached to a rod, which deflect the gases against the sides of the pipes and thus promote cooling. The gases can escape through the pipe  $d$ , though this is dispensed with in Belgian works. The

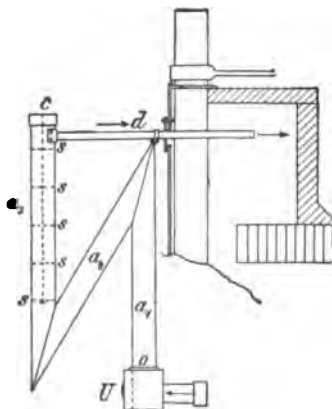


FIG. 103.

gases are best allowed to escape through a hole in the sliding cover  $C$ . It is advisable to lead the gases and vapours from 3 to 5 retorts into one common lower chamber to which is attached an upper chamber (Fig. 104). The lower chambers must be small enough not to hinder access to the retorts, and the upper chambers must be so arranged that inspection is possible. While the upper chambers of the three uppermost rows may have arms of equal length, those of

the other rows of retorts must protrude more the lower their position in the furnace, so that space is obtained for fixing on the upper chambers (Fig. 105).



*Furnaces*

The furnaces employed in distillation are, as already mentioned, shaft furnaces fired externally. The retorts are disposed in them in a number of tiers one above the other, so that the greater portion of their surfaces shall be exposed to the flame. They rest with their back ends on ledges built into the back wall of the furnace, and with their front ends on plates made of clay and iron in the hotter and cooler parts respectively. They slope to the front end so as to facilitate the emptying and the removal of liquids. The number of retorts which a furnace will take varies, according to the dimensions of the latter,

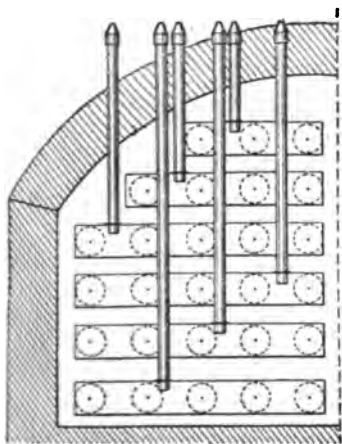


FIG. 104.

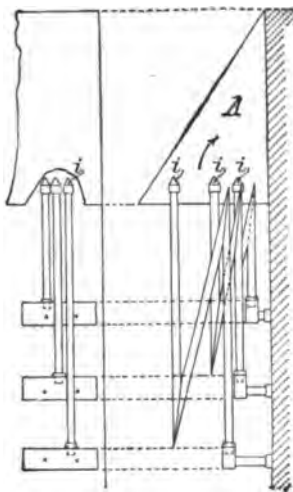


FIG. 105.

between 50 and 1,008. For example, a double furnace in La Salle, in the State of Illinois, has on either side 204 retorts, or 408 altogether. The newer furnaces there have 448, 576, 864, and 1,008 retorts.<sup>1</sup> Furnaces fired with natural gas at Jola, Kansas, have 600 to 660 retorts, arranged in 5 rows, with from 60 to 66 on either side. Furnaces fired with coal in Kansas and Missouri have 2 rows of 112 retorts, or 224 in all. The newer furnaces with Siemens firing at Overpelt, Prayonn, and Engis in Belgium have 240 retorts; those at the older works in Vieille Montagne have 100 retorts in 5 rows on each side, or 200 altogether. Fewer retorts per furnace are to be found in many works, local conditions and the custom of the workmen

<sup>1</sup> Ingalls, *The Metallurgy of Zinc and Cadmium*, 1903.

determining the number. In order to enable the furnaces to hold as many retorts as possible, they have been made oval in cross section, or the front of the furnace has been made of hexagonal frames of cast iron, the end of a retort fitting into each hexagon, or instead of the hexagons cast-iron rings have also been employed. The furnaces are either single, and then consist of one shaft-like chamber filled with retorts, or else are double, in which case they are divided by a vertical partition wall into two shafts, each of which carries retorts. With respect to the mode of firing, furnaces are divided into those fired by means of grates, those fired by grates and gas, and those fired by means of natural gas. By a suitable modification of grate firing (Wetherill grates and modified gas-firing), and more especially by the introduction of gas firing, important advantages as regards the consumption of fuel and economy in retorts have been attained, and the distillation has been rendered independent of the nature of the fuel. Apart, therefore, from exceptional conditions, the method of gas firing should as a rule be used for Belgian furnaces.

We have accordingly to consider:—

1. Furnaces fired by grates.
2. Furnaces fired by grates and by gas.
3. Furnaces fired by producer gas.
4. Furnaces fired with natural gas.

### 1. *Furnaces Fired by Grates*

These furnaces are either single or double. The grates are either flat or step-grates. When long-flaming coals are available, the so-called clinker grate is used, in which the fresh coals are thrown upon a bed of clinker, and the air which enters under the grate is warmed by passage through this bed. The clinker is removed through the interspaces between the grate bars, and falls into the ashpit. A clinker grate has the advantage, as compared with ordinary grates, of consuming effectually the fuel, of heating the air used for combustion, and of only needing the removal of ashes at longer intervals of time, as also of affording a better protection to the grates against the fire. For leaner coals the so-called open grate is used in which ashes are removed from above. Anthracite can be burned on the so-called Wetherill grates. These are in use in Bergen Port and in Bethlehem in the United States. The grates consist of cast iron plates  $1\frac{1}{2}$  inches thick, which are pierced by

conical holes. These holes are 1 inch wide at their wide end, 0·4 inch at the narrow end. There are 100 holes to the square foot. The plates are so arranged upon cast-iron bearers that the narrow ends of the holes are uppermost, thus preventing them from becoming stopped up. Air is introduced by means of a fan blast and conducted by means of a flue passing underneath the floor of the works into the closed ashpit. A further portion of air is heated in the lowest retorts, which are not charged, and is conducted into the fireplace. By this means 7 tiers of retorts can be heated.

### *Single Furnaces*

In these furnaces 11 to 12 retorts are allowed to every 35 cubic feet of furnace capacity, and 1 square foot of grate area to 16 to 20 cubic feet of furnace capacity. The older Belgian furnace—the so-called Liège furnace—was designed in 1807 by Abbé Dony in Liège. Its arrangement, as it was erected at Moresnet, is shown in Figs. 106 and 107.<sup>1</sup> The arched furnace shaft is 10 feet 6 inches high, 8 feet wide, and 5 feet deep. It contains 69 retorts in 9 tiers. The lowest tier of 8 retorts, which lie nearest to the grate, known as *protecteurs*, or “cannons,” is not charged. Their only object is to weaken the cutting action of the flame and to distribute the latter uniformly amongst the other retorts. The remaining retorts are arranged with their back ends upon the projections *v* of the back wall, and with their front ends, in the six lower rows, resting upon tiles (*taques*), *s*, the prolongation of which is formed by plates of iron; in the two upper rows they rest upon plates of iron only. By means of bricks placed on edge the whole front wall of the furnace is divided into compartments, which contain in the topmost row one retort each, whilst in the lower tiers they contain two retorts each. *R* is the grate, *M* the fire door, *N* are the flues, through which the products of combustion escape either into the stack or into the furnace for calcining calamine. *K* is a chamber in which the residues from distillation are collected. The arrangement of the retorts and adapters is shown in Fig. 108. At the Morriston works of Vivian and Sons, near Swansea, in England,<sup>2</sup> there were in 1878 single Belgian furnaces in use, the larger of which contained 6 tiers of retorts, 16 in a row and 1 tier with 16 blanks, or 112 retorts

<sup>1</sup> *Berg- und Hüttenm. Ztg.* 1859, p. 405; 1860, p. 3.

<sup>2</sup> *Borgnet, Berg- und Hüttenm. Ztg.* 1878, p. 388.

altogether. The blank retorts or "*cannons*" were constructed with an air flue in their lower portion in order to cool them, as shown in

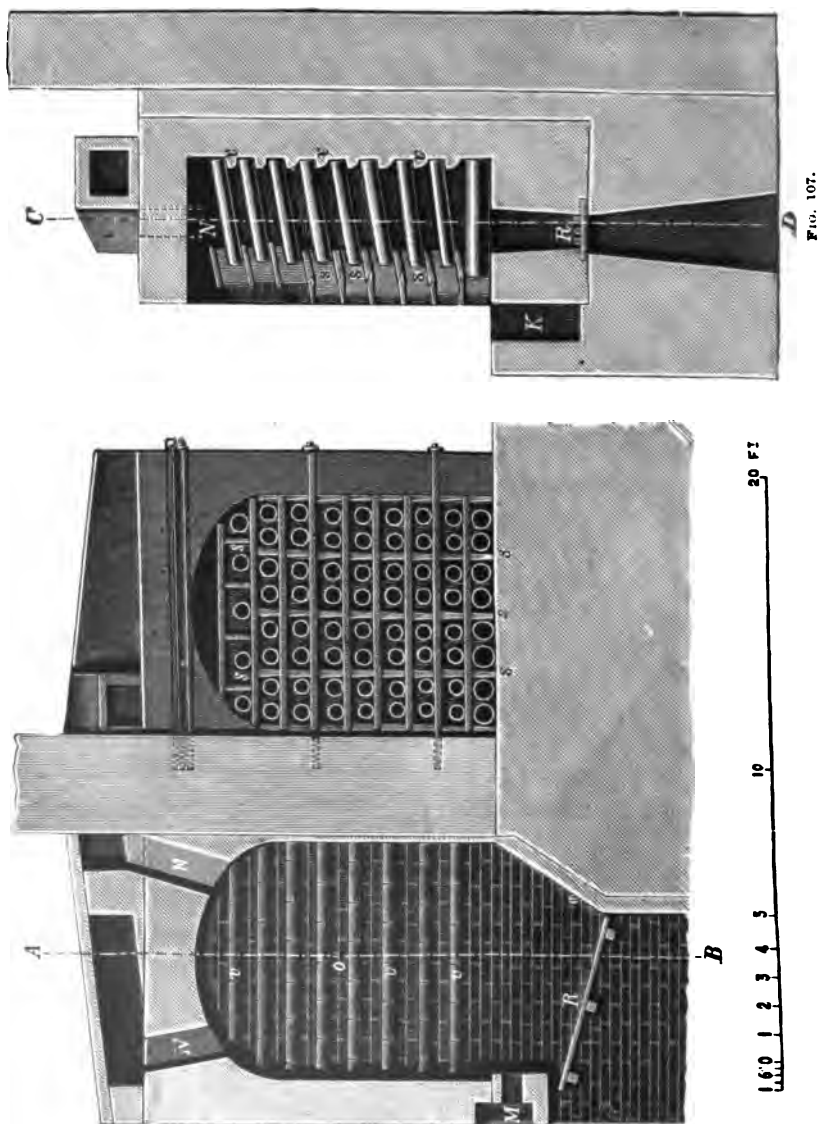


Fig. 109. Each furnace had two fireplaces 6 feet long by 9 inches wide. Each furnace treated two charges daily, but the four bottom tiers only treated one charge each. In 24 hours 27 cwts. of calami

and blende, containing 50 to 51 per cent. of zinc, and 15 cwts. of coal-dust, were distilled, the product being 11 to  $11\frac{1}{2}$  cwts. of zinc. The coal consumption was 2 tons to 1 ton of ore. There were three men employed on each shift. Four retorts were destroyed in every 24 hours. These furnaces were not satisfactory as regards the consumption of fuel and the working costs, and were far surpassed by the Cornwall furnace employed at the same works, designed by Alfred Borgnet. Instead of one single grate running parallel to the longitudinal axis of the furnace, these furnaces possess 5 grates at right angles to the axis, inclined parallel to the direction of the retorts, and capable of being fired from the back side of the furnace.



FIG. 108.

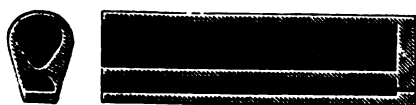


FIG. 109.

consequence of this arrangement, the length of the furnace can notably increased. The construction of these furnaces at the Morrison Zinc Works is shown in Figs. 110 and 111. They contain 10 retorts in 6 horizontal tiers. The retorts *U* of the four lower tiers, the so-called *cannons*, have air flues as shown in Fig. 109, but the retorts of the two uppermost tiers are without such flues. As one of the five grates 24 inches by 6 inches in area. The ducts of combustion pass through 17 apertures in the arch of the furnace into the main flue *S*, and from the latter into a stack 23 feet in height. The front wall is composed of 11 cast-iron plates, cast in one piece, each of which is 4 inches broad and has a 0.4 inch thick. The interspaces between the walls are filled with fireproof material. Cast-iron plates 1 foot 8 inches long slide

in grooves along the pillars, and upon these lie fire-brick tiles, upon which the front portions of the retorts may rest. The length of the furnace between the outer walls, which are 4 feet thick, is 20 feet 6 inches, the width, including the brickwork, is 7 feet, the height from the grate to the arch is 14 feet, the height in front from the first cast-iron plate to the spring of the arch is 10 feet. The

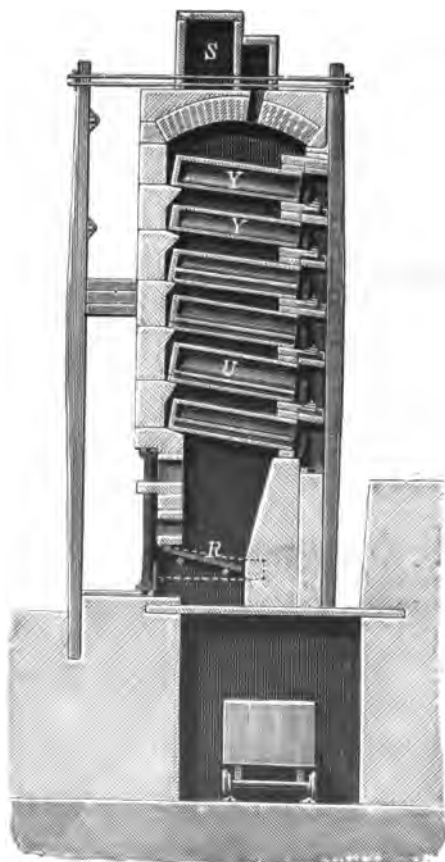


FIG. 110.

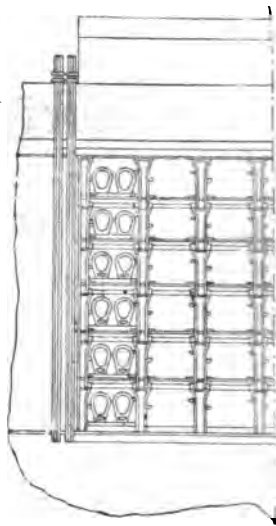


FIG. 111.

distance between the cast-iron plates of the first and second tiers amounts to 20 inches, of the third and fourth tiers to 19 inches, of the fifth and sixth tiers to 17 inches. The recesses are 20 inches wide, and carry 2 retorts each. The arch consists of alternate layers of the best fire-brick and Dinas brick, and is 10 inches thick. The furnace is supported upon iron rails. It is capable of treating

2 tons 2 cwts. of ore containing 49 to 50 per cent. of zinc, mixed with 1 ton of coal, in 24 hours, the output being  $15\frac{1}{2}$  to 17 cwts. of zinc. For 1 ton of ore 2 tons of fuel and 1.6 retorts are consumed.

The Belgo-Cornwall furnace<sup>1</sup> contains 4 tiers, each of 10 oval *cannons* or dummy retorts, and two rows of 18 retorts each. The grates are not transversal, but longitudinal, there being two, each of 8 feet 6 inches by 10 inches area. These furnaces treat in 24 hours 30 cwts. of ore mixed with 9 cwts. of coals, with an output of  $12\frac{1}{2}$  to 13 cwts. of zinc. Each ton of ore requires the consumption of 42 cwts. of coals as fuel. A furnace destroys 4 retorts per day. Compared with the older Liège furnace, the Cornwall furnace requires less labour and is far more durable, lasting 5 to 6 years, as compared with 12 to 15 months. On the other hand, it requires more coals than does the Liège furnace, due in part to the cooling of the retorts. The Belgo-Cornwall furnace requires, on the other hand, more labour, but consumes fewer retorts than does the Cornwall furnace. It is somewhat inferior to the latter, but far superior to the old Liège furnace. A furnace with gas firing, on the Siemens principle, has been patented by the *Actiengesellschaft für Glas-industrie*, (late Friedrich Siemens), of Dresden.<sup>2</sup>

It is not known whether this furnace has ever come into use.

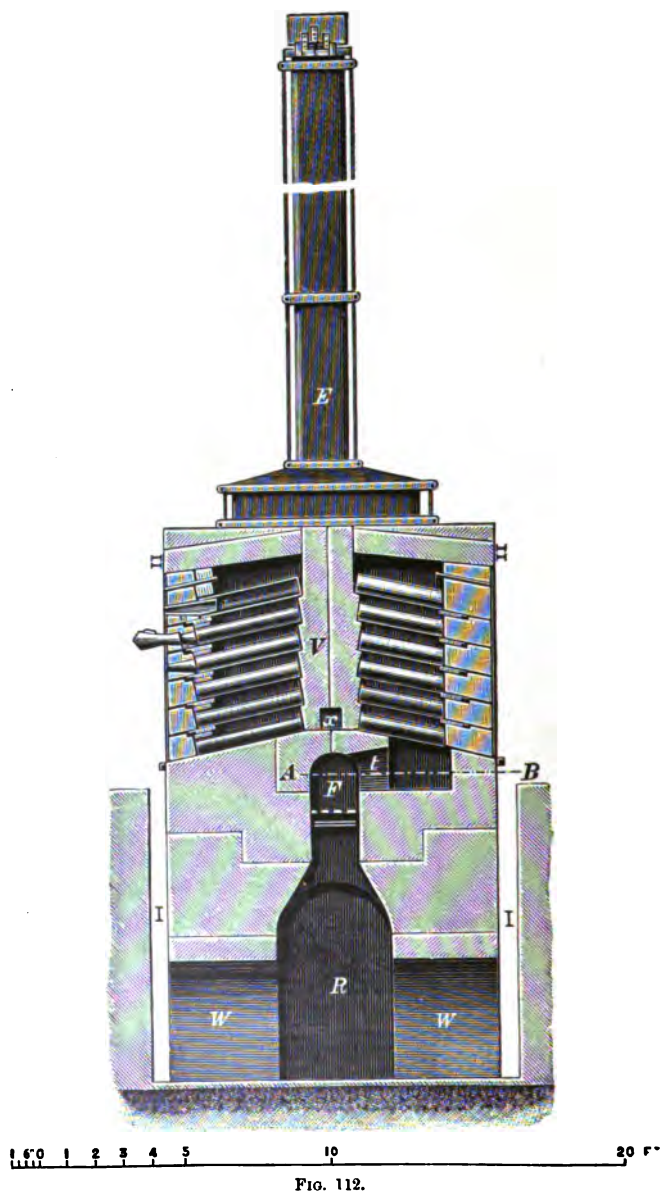
### *Double Furnaces*

As an example of the double furnace with grate fire, the furnace which was in use in the year 1871 at the works of the Nouvelle Montagne, at Prayon, may be described. Its construction is shown in Figs. 112 to 114.<sup>3</sup> In these *V* is the vertical wall which divides the furnace into two parts. It also serves to support the rear ends of the retorts, the front ends of which are carried by slabs in the same way as in the single furnace. Each half contains 46 retorts in 6 tiers, the lower 5 rows consisting of 8 retorts each, whilst the upper one contains only 6. *F* is the fireplace with flat grate, the arch of which carries the above mentioned dividing wall. Above the arch there is an air flue for the purpose of cooling the brickwork. On either side of the arch there are slots *t* at given distances apart,

<sup>1</sup> *Berg- und Hüttenm. Ztg.* 1878, p. 387.

<sup>2</sup> D. R.-P. No. 50917, September, 1889.

<sup>3</sup> Massart, *Rev. Univers. des Mines*, 1871, vol. xxix. p. 313; *Zeitschr. d. Ver. Deutsch. Ing.*, vol. xvi. pp. 10, 165.



through which the flame enters both divisions of the furnace. In each division there are 2 flues *z*, in the arch of the furnace, through which the products of combustion pass into stacks *E* 23 feet in height. The residues after distillation are discharged



through the flue *I* into the vault *W*, and removed by means of the arched gallery *R* running beneath the grate. The double furnaces at Kansas and Missouri have 112 retorts in 7 rows on each side, that is, 224 in all. For further information upon grate-fired Belgian furnaces in the United States see Ingalls, *The Metallurgy of Zinc and Cadmium*, p. 133.

## 2.—Furnaces Fired by both Grates and Gas

Hauzeur has designed a peculiar form of double furnace, fired both direct and by means of gas, which has been used in Belgium and Spain.<sup>1</sup> The retorts of one division are heated by means of

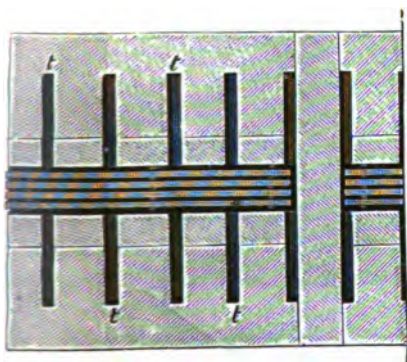


FIG. 113.

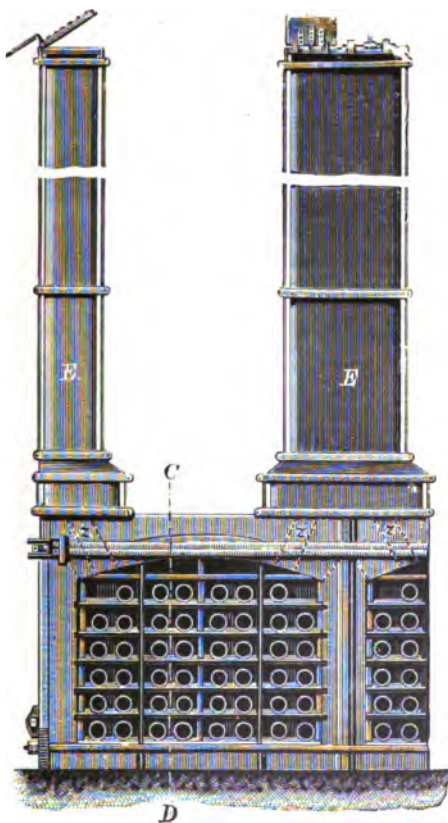


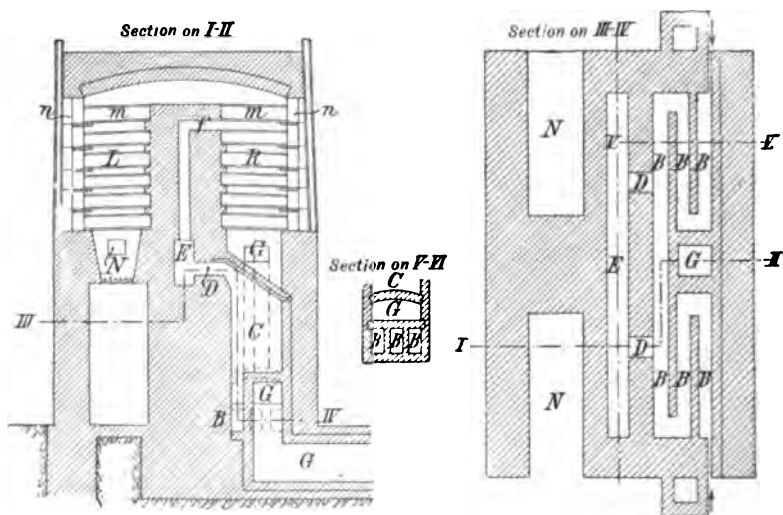
FIG. 114.

direct firing. The products of combustion, mixed with unburnt gases, escape at the upper end of this division and enter the second division, which they traverse from above downwards; in the second division the unburnt gases are completely burnt by the introduction of heated air. The construction of this furnace, which thus presents a combination of grate and gas-firing, is shown in Figs. 115 to 117;<sup>2</sup> *N* is the grate, upon which the fuel is only partly burnt by the introduction of a limited amount of air.

<sup>1</sup> D. R.-P. No. 3729, September 15, 1877.

<sup>2</sup> Spirek, *Oesterr. Zeitschr.* 1881, p. 335; Dingler, 235, 221.

The flame and unconsumed gas traverse the first division *L*, and then enter the second division *R*, in which the unburnt gases are completely burnt. The air required for this purpose enters the second division by means of flues *B, B*, in the walls of the furnace, passes out of these into the chamber *C*, thence passes through the horizontal flues *D* into the flue *E* in the central wall, escaping finally in a heated state through the horizontal apertures *f* into the upper part of the shaft *R*, where the unconsumed gases are completely burnt. The products of combustion descend in this



Figs. 115—117

shaft, escaping through the flue *G* into the stack. On their way they give off a considerable portion of their heat to the brickwork surrounding the air flues.

### 3.—Gas-fired Furnaces

These furnaces are heated entirely by means of producer gas. They have the advantage, as compared with direct fired furnaces, of being independent of the nature of the fuel, of consuming less fuel and fewer retorts, and of extracting more zinc. The diminished consumption of retorts depends not only upon the uniform temperature obtained by means of gas-firing, but also upon the existence of a slight plenum of pressure in the furnace, which prevents cold air from entering it, whereas in a grate-fired furnace cold air enters the

latter whenever fresh fuel is charged. In consequence of these conditions, the retorts are less apt to crack, and last longer. For the same reason the output of zinc is higher, because less zinc vapours escape from the retorts into the furnace. The air used for burning the gas should, as a rule, be heated. Gas furnaces with and without regenerators are employed. Furnaces with regenerators, although they consume less fuel and attain higher temperatures than the others, have been employed in but few cases. Only in recent years have these furnaces been improved and more generally adopted.

### *Gas-fired Furnaces without Regenerators.*

These furnaces have been used at Moresnet, in Belgium, and in the United States of North America. At Moresnet, generators with step grates as well as Gröbe-Lürmann producers have been employed.<sup>1</sup> The latter form of producer has given results inferior to those obtained by the step grates. Two furnaces were united to form one block, but each furnace was provided with a separate producer. The two furnaces were not built directly back to back, but a flue, into which the products of combustion escaped, separated them. The gases entered the furnace from the producers, when they came into contact with hot air heated in the bottommost row of the retorts, and were thus burnt. They ascended in the furnace and escaped from the upper end thereof into the above-mentioned vertical flue, through which they made their way downwards towards the stack. The furnaces used in the neighbourhood of Liège<sup>2</sup> are broader than they are high. They are built in pairs back to back, each separate furnace being provided with two gas-producers. The air is heated and is caused to enter the furnace at various places in order to heat the latter as uniformly as possible. Loiseau<sup>3</sup> passes producer-gas through a series of chambers leading one into the other and filled with retorts. Into the first heating chamber he admits cold air, into the following ones hot air, the temperature of which is gradually raised in proportion as the amount of combustible gases in the current diminishes. The object of this arrangement is to attain as uniform a temperature as possible in all portions of the furnace, so that loss of zinc, due to alternations of temperature, may be avoided.

The construction of the older type of gas-fired furnace at the Matthiesen-Hegeler Zinc Works, at La Salle, is shown in Figs. 118

<sup>1</sup> *Allgemeine Hüttenkunde*, p. 213; *Wochenschr. d. Ver. Deutsch. Ing.* 1877, p. 14.

<sup>2</sup> *Wochenschr. d. Ver. Deutsch. Ing.* No. 44.

<sup>3</sup> *Berg- und Hüttenm. Ztg.* 1879, p. 171.

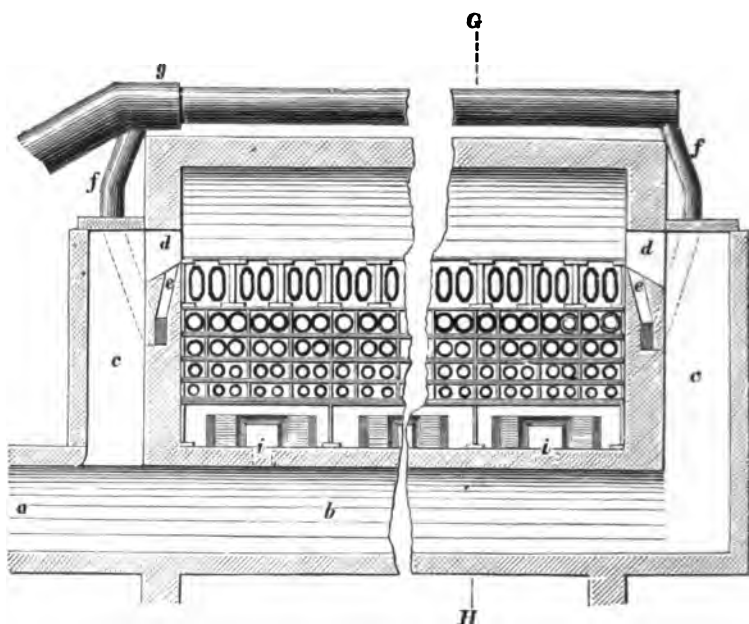


FIG. 118.

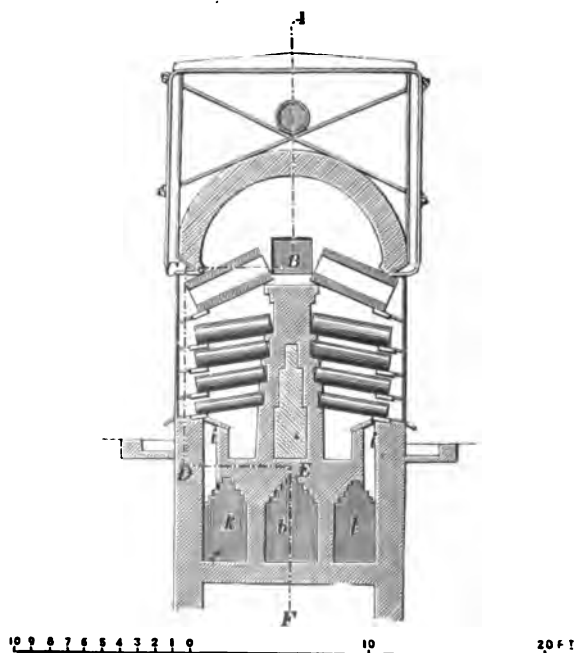


FIG. 119.

and 119. The furnaces are double furnaces into which the gases enter from above. The topmost tier contains 36 retorts. These are 4 feet 3 inches long, 20 inches high, and 8 inches broad in the clear; below these there are 4 tiers of 42 retorts each, the length and diameter of which decrease from above downwards. Each side of the double furnace accordingly contains 168 retorts, not counting those in the topmost tier. The gases are generated in producers provided with step grates, not shown in the illustration. Passing into the horizontal flues *b*, they enter the vertical flues *c*, on either side of the furnace, and escape through the upper end of the latter through the slots *d* into the upper portion of the furnace. They are here burnt by means of a blast of air which enters the furnace through the blast main *G*, *g*, by the tubes *f* and the slots *e*. The flame thus produced traverses the furnace from above downwards. The products of combustion escape through *i* into the flues *k*, *l*, to the stack. A portion of the heat of these gases penetrates through the walls of the flue *b*, and thus warms the gases entering the furnace.

The modern furnaces at the above-named works<sup>1</sup> consist of a row of heating chambers communicating with each other, which are traversed in turn by the stream of gas, and are furnished with apertures for the introduction of hot air. Each pair of furnaces has a back wall in common, and is united to form a block. There are 4 to 6 tiers of retorts in each furnace, each row consisting of 56 to 72 or 84 retorts. The largest block of two furnaces contains 1,008 retorts.

A furnace designed by Hegeler,<sup>2</sup> which has not yet come into use, is shown in Figs. 120 and 121. It can be fired with natural gas. The air enters at one end of the furnace, and the gas is led in through pipes at different positions along the front of it. The retorts are arranged in groups, each of which receives fresh gas, so that all parts of the furnace are at the same temperature. The air is forced by a fan into a sheet-iron flue *B'*, which is provided with a regulator *b'*, and passes thence into the upright flue *B* made of fire-brick, and from this into the retort chamber of the furnace. The retorts are arranged in groups, and these groups are separated from one another by the spaces *D*. The gas passes at suitable pressure through the pipe *E'* into the upright branch pipes *e e*, and issues from these through the hole *c'* in the front wall of the furnace into the spaces *D* between the groups of retorts. Some gas also enters the air-flue *B* through the pipe *c'* and its branch *C'*. The

<sup>1</sup> D.R.-P. No. 10009, October 19, 1879.

<sup>2</sup> U.S. Pat. No. 612104, October 11, 1898.

quantity of gas entering through  $e$  and  $e'$  is controlled by a regulator.<sup>1</sup>

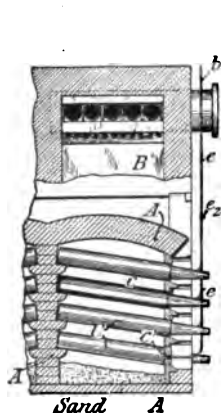


FIG. 120.

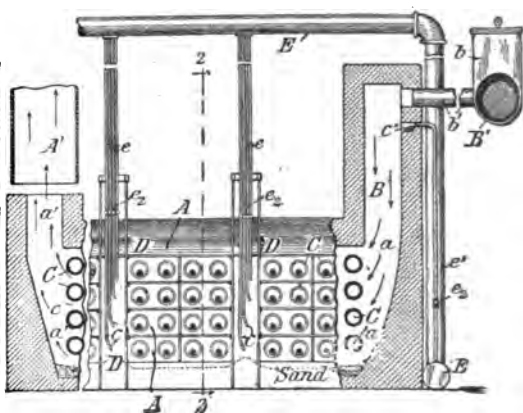


FIG. 121.

A gas-fired furnace for the treatment in retorts of zinc ores rich in lead has been designed by Thum, but does not seem to

have proved satisfactory in practice. The retorts of these furnaces, shown in Fig. 122, lie at a steep angle, and are open at both ends.<sup>2</sup> They are charged from below and closed at their bottom end by a clay plug. The lead collects in the bottom portions of the tubes  $C$ , whilst the zinc vapours escape at the upper ends and are there condensed by means of suitable adapters. The gases generated in the producers enter the furnace through the flue  $V$  by means of a slot  $y$ , and here mix with air entering through the slots  $x$ ; the products of combustion escape through the flue  $z$  into the flue  $t$ , whilst the air

entering through the flues  $r$  is heated by the gases escaping through the former. Furnaces with inclined retorts open at the lower end.

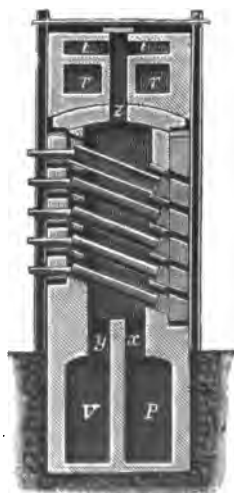


FIG. 122.

<sup>1</sup> Stölzel, *Metallurgie*, p. 799; *Berg- und Hüttenm. Ztg* 1875, p. 1.

<sup>2</sup> *Ibid.*

which allow the lead to flow away continuously, have been devised by Schneider.<sup>1</sup> Holstein has described furnaces with only one retort, from the lower end of which the lead can be tapped.<sup>2</sup> Nothing is known as to the application of these furnaces.

### *Gas-fired Furnaces with Regenerators*

To this class belong the furnaces of Siemens, Neureuther, Ferraris, Dor, and Convers and de Saulles. Belgian furnaces fired on the Siemens principle were for a long time but exceptionally used, since the working results did not come up to anticipation. Only recently has their application become more extended. Thus they are used at many Belgian works in place of the old furnaces with grate firing. At Overpelt, Prayon and Engis they are in use, each furnace having 240 retorts in a block. In the United States they have been constructed at Rich Hill, Pittsburg, and Peru, though only in Peru have they continued working. The construction of an older Belgian furnace on the Siemens principle is shown in Figs. 123 and 124.

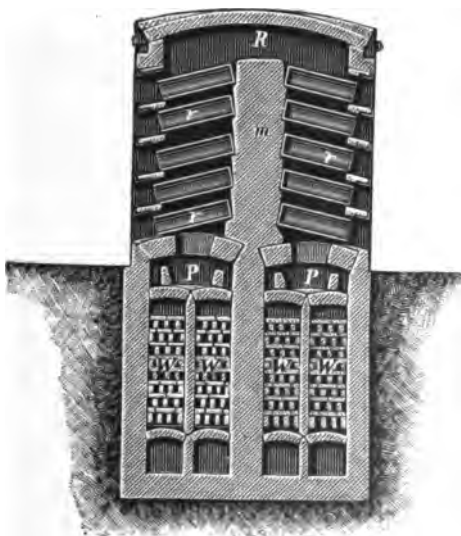


FIG. 123.

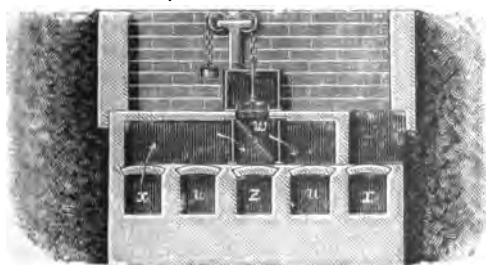


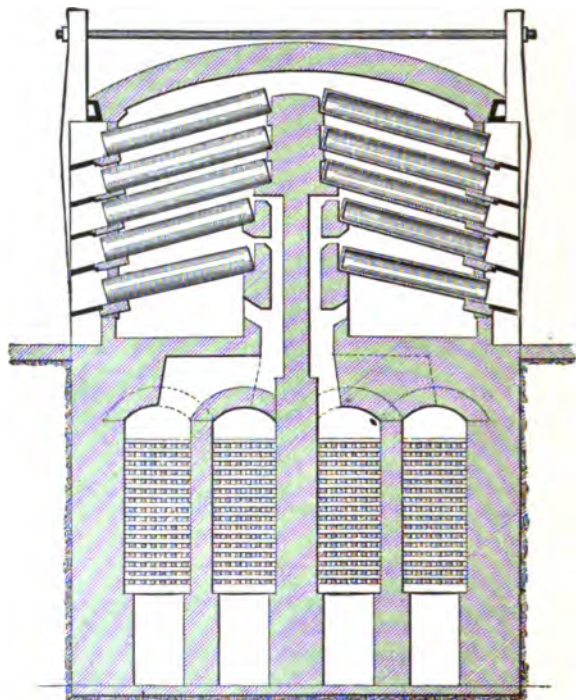
FIG. 124.

The furnace is double;  $r, r$  are the retorts,  $W, W$  the regenerators. The external pair of regenerators are gas regenerators, the inner ones air regenerators. The gas and air mix in the chambers  $P$ , the

<sup>1</sup> U.S. Pat. No. 605802, June 14, 1818.

<sup>2</sup> U.S. Pat. No. 554185, February 14, 1896.

burning gases ascend one shaft, descend through the other, and traverse the regenerators lying below the latter on their way to the stack. After a certain interval—about half an hour—the direction of the air and gas currents is reversed. The burning gases then ascend in the second shaft and descend in the first, escaping to the stack through the second pair of regenerators. The gas current is reversed by the valve *w* (Fig. 124), which alternately connects the entering gases with one of the gas-flues *x* and the products of combustion with the flue *z* leading to the stack. A similar reversing



NEUBRUTHER-SIEMENS REGENERATIVE FURNACE.

FIG. 125.

valve, not shown in the figure, serves to reverse the air current as required. Such a furnace with 120 retorts on either side, 10 tiers of which are charged and 1 blank, is in use at the works of the Illinois Zinc Company at Peru, near La Salle.

Arrangement of the retorts into separate groups has been proposed by the *Actiengesellschaft für Glas-industrie* (late Friedrich Siemens) in Dresden,<sup>1</sup> the gas and air inlets being in the furnace bed at one side, and the outlets for the products of combustion at

<sup>1</sup> D. R.-P. No. 50917.



the other side of the furnace; this arrangement is said to give better firing results from the freer expansion of the flame, and it has advantages also when solid fuel is used.

The furnace of Neureuther<sup>1</sup> (Fig. 125) is an improved Siemens furnace, differing from the latter in that the mixed gas and air, instead of entering under the lowest tier of retorts, is distributed

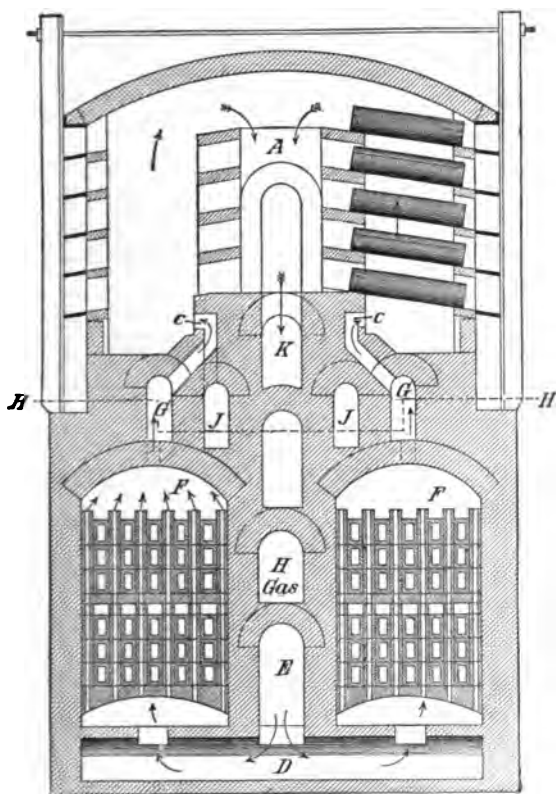


FIG. 126.

by flues in the middle wall of the furnace and comes into the furnace in several streams at different heights. This arrangement is said to produce a more uniform heating of the retorts.

The furnace of Ferraris has only air regenerators, and is divided into two parts by a wall running along the longitudinal axis. Each division is traversed lengthways by the burning gas, and as the current is reversed from time to time, the furnace, even at the ends, becomes uniformly heated. There are two air regenerators under each furnace division through which the burnt gas and the air pass. Each re-

<sup>1</sup> U.S. Pat. Jan. 22, 1901, No. 666390.

generator is divided into two compartments by a horizontal partition, and through these pass, alternately, the burnt gases downwards, the air for combustion upwards. The producer gas leaves the producer hot through a suitably lined pipe, and is further heated by passing through flues in the middle wall of the furnace; it then reaches alternately each end of the furnace, whence it passes into the furnace itself through a row of inlet holes in the corresponding half of the furnace division. The gas mixes with air heated in the regenerator, and the burning mixture is drawn the length of the furnace, and escapes through the regenerator into the stack. After an interval

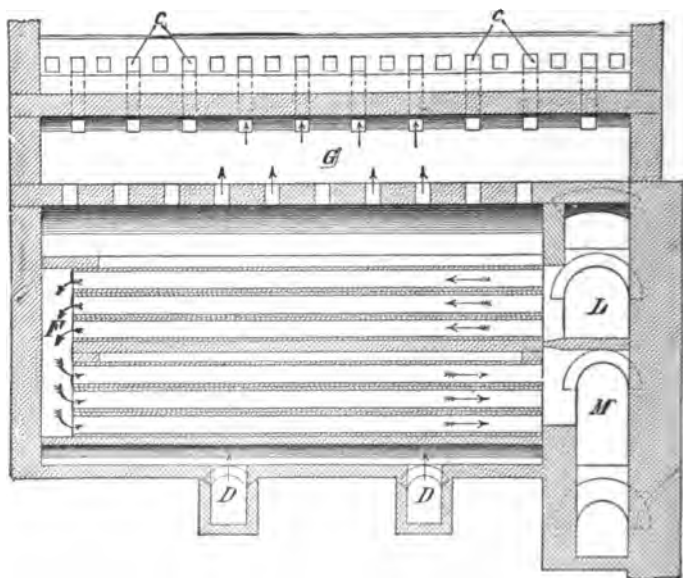


FIG. 127.

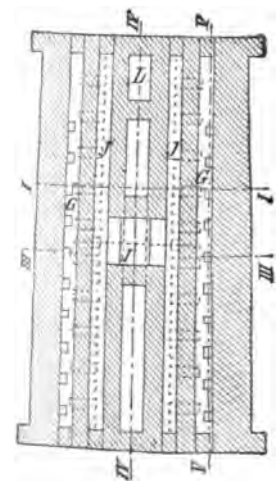
of time the stream of gas is reversed. The furnace has 180 retorts in one block, and works off 6 to 7 tons of calcined ore in 24 hours.

The furnace of Dor has the regenerators at both ends of the furnace.<sup>1</sup> That of Convers and De Saulles<sup>2</sup> has only an air regenerator. The construction of the latter is shown in Figs. 126—130, of which Fig. 126 represents a vertical section along the line *II* of Figs. 128 and 129; Fig. 127 a longitudinal section through the regenerator along the line *VV* of Fig. 129; Fig. 128 a horizontal section along the line *HH* of Fig. 126; Fig. 129 a vertical section along the line *III*, *III* of Fig. 129; and Fig. 130 a vertical section along the line *IV*, *IV* of Figs. 128 and 129. The scale in Figs. 128—130 is nearly half that

<sup>1</sup> Brit. Pat. No. 22694, 1891.

<sup>2</sup> U.S. Pat. No. 712502, November 4, 1904.

of the others. The producer gas passes from the generators through the flue *H* and the upright flue *I* into the flues *J J* and *d* (Fig. 129) into the furnace. The air for combustion passes through the flue *E* and those beneath it, *D*, and from these into the upright channels of the regenerator in which it is pre-heated by the products of combustion escaping from the furnace. The heated air passes next into the upper chamber of the regenerator *F F* and is led through the flues *G*, and the sloping branches leading from these, to the openings into the furnace *C*. These openings serve alternately for the admission of air and gas (Fig. 127). The products of combustion leave the furnace at *A* and are led through the flues *K* and *L* into the horizontal passages of the two regenerator chambers *F F*, which they traverse in the direction of the arrows (Fig. 127). Thence they



FIGS. 128 and 129.

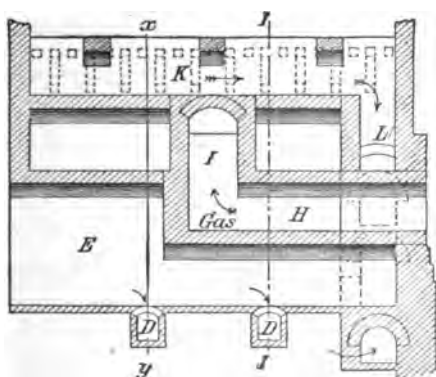


FIG. 130.

escape into the stack through the flue *M*. The gas gets strongly heated in the flues *J J*, which are kept at a red heat. These furnaces are said to yield good results.<sup>1</sup>

#### 4.—Furnaces fired with Natural Gas

These are in use in Jola and Cherryvale, Kansas, and Marion, Indiana, in the United States.<sup>2</sup> In Cherryvale draught is produced

<sup>1</sup> Ingalls, *op. cit.* p. 472.    <sup>2</sup> *The Mineral Industry*, 1900, p. 651 ; 1902, p. 667.

by chimneys. The furnace is double, each half holding 100 retorts arranged in 5 rows of 20 each. Gas is led in through iron pipes under 4 ounces pressure, and traverses the furnace from end to end, escaping at the end opposite to the inlet. In Jola artificial draught has superseded draught produced by stacks. The furnaces are double, and contain in all 600 to 660 retorts, which are disposed in 5 rows of 60 to 66 in each half. The arrangement of these furnaces

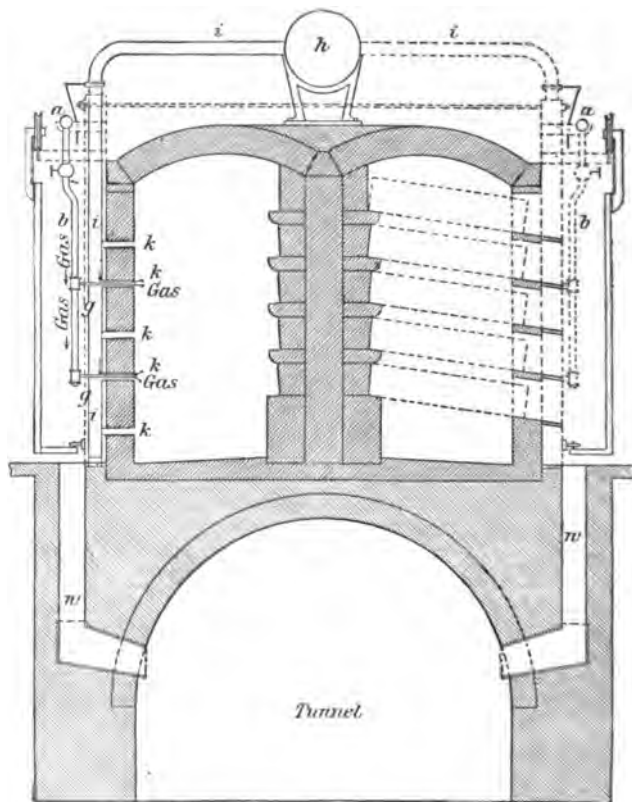


FIG. 131.

is similar to that of the newer furnaces at La Salle, the gas being led in at 4 to 6 ounces pressure through branch tubes from the main pipe. The inlet holes are arranged at different positions along the front of the furnace, where the gas is mixed and burns with air supplied by a blower.

The arrangement of the newest furnaces at Jola is shown in Figs. 131 and 132.<sup>1</sup> Fig. 131 represents a vertical section through

<sup>1</sup> Ingalls, *op. cit.* p. 481.

the furnace, the left half of the cut being through the pillars and the gas and air pipes, and the right half through the middle of the

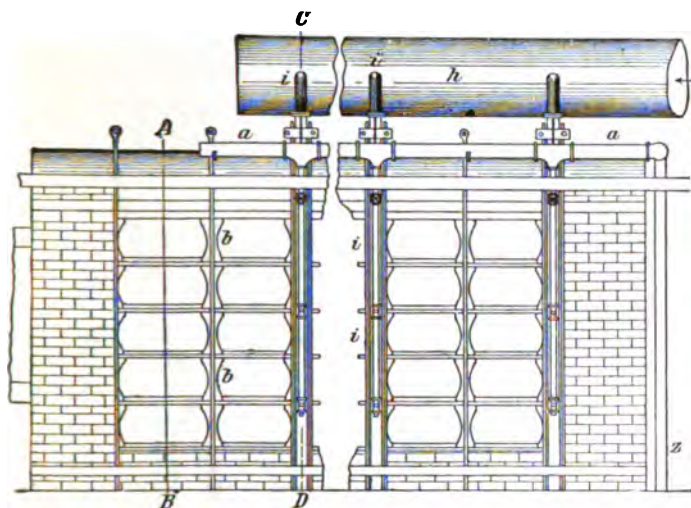


FIG. 132.

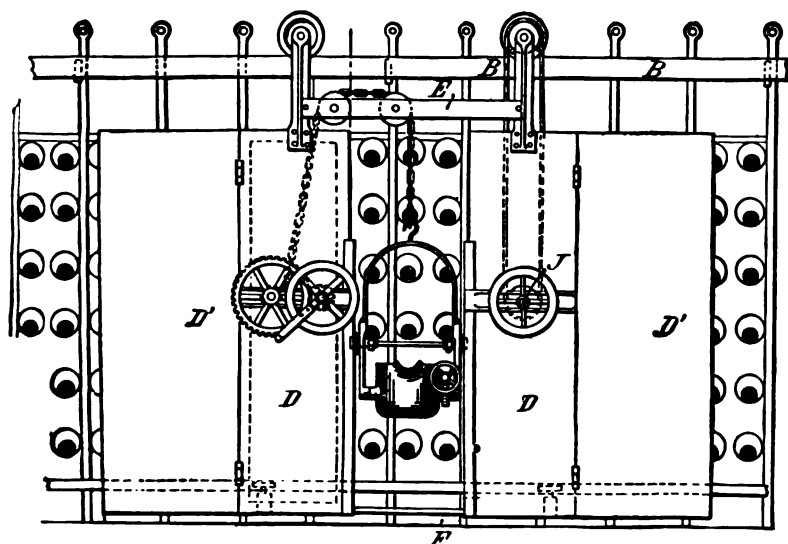


FIG. 133.

furnace between two pillars. Fig. 132 is a view of the front of the furnace, without the retorts. The gas is driven under pressure through wrought-iron pipes into the horizontal pipes *a*, which run

the length of both halves of the furnace, and are connected to the upright pipes *z* coming from the regulators. Thence it passes through the upright pipes *b* and the horizontal pipes *g* into the furnace. The air enters through inlet holes and passes through the pipe *h* and its branches *i* and *k* into the furnace. The retort residues are shot down the channels *w* into a tunnel under the furnace.

The double furnaces at the works of the Lanyon Zinc Co., built on the pattern of the Jola furnaces, have 400 tubes arranged in 5

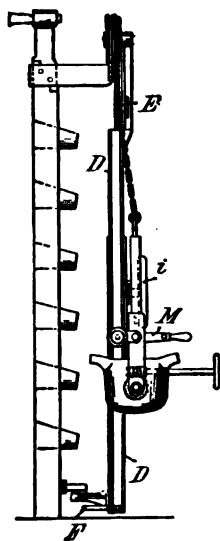
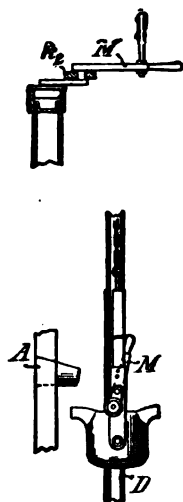


FIG. 134.



FIGS. 135 and 136.

tiers of 40 each on either side. They are said to have given good results.

All these furnaces have movable shields to protect the workmen during charging and emptying the retorts and removing the zinc from the adapters, so as to facilitate these processes.

The construction of a Chapman shield or protector as used in the Jola region, is shown in Figs. 133—136, the front view being represented in Fig. 133 and the side view in Fig. 134. This appliance consists of two upright plates *D D'* made of steel or sheet iron, between which hangs on bearings a ladle with two lips. This can be moved up and down, and serves to collect the molten zinc. The shield can be moved along the front of the furnace, being hung for this purpose on two wheels which run along the rail *B*. Movement is imparted by turning the handwheel *J*, which is connected by a chain to one of these wheels. The lower end of the shield is kept at a suitable distance

from the furnace by means of the horizontal rod *F* and a roller fastened to it which works under a horizontal rail. The appliances for raising and lowering the ladle by means of the chain, wheel, and roller are shown in Fig. 133. To guide the ladle, there are rollers at the end of the lever *M* which work in corresponding slots in the plates. When the lever is depressed, during the raising and lowering of the ladle, the latter is drawn so far back that it does not come in contact with the ends of the retorts (Fig. 135). During the pouring of the zinc from the adapters, the ladle is in the position shown in Fig. 136. When full of zinc the ladle can be tipped by turning a handwheel which actuates a rack and pinion. The ladle can be removed from the shield when the residues are withdrawn from the retorts.

Lanyon has patented another shield, for which see U.S. Patent No. 621577, March 21, 1899.

### *Mixing the Charge*

As already stated, the ores, when various kinds are on hand, are so combined that the impurities thereof unite to form compounds which shall neither melt nor form fusible compounds with the material of the retorts at the temperature of distillation, whilst a moderately high output of metal shall result. Silicate of zinc needs no special additions, because when finely ground it is reducible by coal alone. Blende, silicate of zinc, and zinc-bearing residues are charged in the form of fine powder; calamine, on the other hand, which is easily reducible, in coarser grains. According to their zinc contents, these ores are mixed with from 40 to 60 per cent. of their weight of lean coals, or small coke, or a mixture of equal portions of coal and coke. Gassy coal should be avoided, because some heat is absorbed in driving off the gas, and because the gases evolved dilute the zinc vapours, and thus make the condensation of zinc more difficult. Blende being more difficultly reducible than calamine, requires a larger admixture of coal. The ground materials are either mixed in troughs, or else in pug mills, or by means of rollers, in which last case, as in North America, a re-crushing of the mixture takes place. The charge is slightly moistened to prevent its being blown out from the retorts by the gases evolved at the commencement of distillation. Binon and Grandfils prefer to mix the charge with tar and press it into blocks before introducing it into the retorts. Schulte<sup>1</sup> mixes the ore with 3 to 5 per cent. of tar before adding the coal.

<sup>1</sup> U.S. Pat. No. 118222, January 13, 1903.

*The Process of Distillation*

When a furnace is to be started, it is gently fired for some days with empty retorts; afterwards the retorts are charged, and the heat gradually increased. The first charges are light, and are gradually increased, until at the end of 14 days the normal rate of working has been attained. The charges are introduced into the retorts, after the adapters have been removed, by means of a scoop shaped like a semi-cylinder attached to the end of a long rod. The retorts which are exposed to the greatest heat receive heavier charges than those less strongly heated. The latter are charged with easily reducible substances such as zinc fume and zinc-bearing residues, as also with poor ores that sinter readily. In modern furnaces the average charge of a retort amounts to 63 lb. of ore. After the retorts have been charged, the adapters with their supports are attached and the space between the adapter and retort is luted with clay. Some time after the retorts have been charged, a flame of burning carbon monoxide escapes from the adapters, which shows after some time the brilliant light of burning zinc vapours. As soon as this phenomenon is perceived, nozzles are attached to the adapters in order to avoid loss of zinc. Although the adapters rapidly attain the necessary temperature, no fluid zinc condenses in them at first, zinc oxide being formed in consequence of the carbon dioxide and water vapour present in the gases. Moreover, on account of their great dilution the vapours of zinc do not condense to a liquid, but form fume. It is only after the above-named gases have disappeared that the zinc vapours begin to condense to liquid zinc. If the furnace works too hot, whereby the formation of considerable quantities of zinc fume in the nozzles is caused, due to imperfect condensation of vapours in the adapters, a few small holes are made in the clay luting. The zinc condensed in the adapters is removed either several times during the process, or only once after its completion. In this case the nozzles are removed from the adapters and the zinc is drawn by means of a rake out of the adapters into ladles held beneath them, from which it is cast in iron moulds into slabs weighing 40 to 44 lb., the surface of the zinc being first skimmed. The time of distillation depends upon the size of the retorts and of the furnaces, upon the position of the retorts in the latter, and also upon the reducibility of the charges and averages between 12 and 24 hours. After its conclusion, the adapters are removed and the residues remaining in the retorts are drawn out by means of suitable rakes. After any accretions have been removed, the retorts are charged again. Damaged retorts are



changed after the conclusion of the distillation. The time occupied in charging, clearing the retorts, repairing the latter, and replacing damaged retorts, depends upon the size of the furnace and the number of retorts it contains.

The same conditions control the number of men required at the furnace. For modern Belgian furnaces, the retorts of which contain on an average 63 lb. of ore, one man is reckoned to every 14 retorts per 24 hours, or in the case of the newer furnaces, one man for 25 to 33 retorts during the cycle of operations (charging and withdrawing).<sup>1</sup> The extraction of 1 ton of zinc from ores containing 50 per cent. of metal requires 5·8 men per 24 hours. The charge of a furnace depends upon the number of retorts in it, and varies between 8 cwts. and several tons of ore. The consumption of fuel varies with the quality of the coal and the method of firing, between 1½ and 2 tons for each ton of ore. The durability of the retorts depends upon the quality of the materials employed and upon the method of manufacture. Modern retorts made by hydraulic pressure last at present upon an average 40 days. The loss of zinc, which was formerly up to 27 per cent. of the contents of the ore, varies with modern furnaces between 10 and 15 per cent.

#### *Examples of Zinc Extraction in Retort Furnaces*

The commercial results attained with modern furnaces fired by gas are far more favourable than in the case of the older furnaces. For the production of 1 ton of zinc from ores containing 50 per cent. of metal, 3 to 4 tons of coal for heating and reduction, and 4 cwts. of clay are required, 2·5 per cent. of the retorts being destroyed daily. With the oldest furnaces 7 to 8 tons of coals were consumed for each ton of zinc. The zinc losses amount to 10 to 15 per cent.<sup>2</sup>

The double furnaces at the works of the Vieille Montagne Company at Angleur contain 100 retorts on either side, a block of furnaces containing 400 retorts. They are fired by means of gas and hot air. Each retort receives a charge of 66 lb. of ore and 26·5 lb. of coal, and produces in 24 hours from 26 to 33 lb. of zinc, together with a certain quantity of zinc fume. For the extraction of 1 ton of zinc 3·5 to 4·5 tons of coal are consumed for fuel and reduction. The

<sup>1</sup> Ingalls, *op. cit.* p. 516.

<sup>2</sup> For further information see Firquet, *Annales des Mines de Belgique*, 1901. VI. I. and II.).

loss of metal amounts to 15 per cent. ; the retorts last from a fortnight to four months, according to their position in the furnace and the care used in their manufacture. A furnace lasts two to three years.<sup>1</sup> The newest furnaces contain 320 elliptical retorts arranged in 4 tiers.

Of the older types of furnace, the Liège furnace with 70 retorts fired by means of a grate, and the grate-fired double furnaces with 92 retorts of the Nouvelle Montagne, at Prayon, may be mentioned, the results quoted having been obtained in the seventies. The Liège furnace was 5 feet deep, 8 feet 6 inches broad, and 9 feet 10 inches high, and contained 70 retorts each 3 feet 3 inches long, with 9½ inches outside and 7½ inches inside diameter, and treated in 24 hours 26 cwts. of charge with a consumption of 14 cwts. of coal for reduction and 2 tons of coal for fuel, the ores containing 47 to 48 per cent. of zinc. The output of a furnace per 24 hours amounted to 9½ to 9½ cwts. of zinc ; the loss of zinc, including that left in the residues, amounted to 18 per cent. Residues containing more than 6 per cent. of zinc were concentrated by dressing, and then treated either in the upper retorts of a Belgian furnace for the extraction of zinc, or in a reverberatory furnace for the production of zinc white. The double furnace of the Nouvelle Montagne Company, at Prayon,<sup>2</sup> with 92 retorts, already described, was charged with 8 cwts. of ore (calamine and blende) containing 40·32 per cent. of zinc, 160 lb. of rich residues from the zinc works, such as zinc fume and skimmings, and 366 lb. of coal for the reduction, during the day shift. On the night shift the furnace worked hotter and was charged with 10 cwts. of ore. The charge was distributed as follows :—

	lb. of ore.	lb. of coal.	lb. of residues.
Retorts of the bottom tier . . . . .	24½	6½	—
Retorts of the third tier . . . . .	37½	6	—
Retorts of the fourth tier . . . . .	16½	8	6½
Retorts of the sixth tier . . . . .	11	11	11

Charging the retorts occupied 3¼ hours. The residues left after distillation in the upper retorts contained on an average 9·15 per cent. of zinc, those in the middle tiers 4·67 per cent. of zinc, and those in the lower tiers 2·28 per cent. The loss of zinc amounted to 11·28 per cent. The retorts in the topmost row lasted for 90 days, those in the bottom row only for 6 days. The furnace campaign lasted 150 to 180 days. As will be seen, these older retort furnaces fired by means of grates were markedly inferior to the modern furnaces both as regards their durability and capacity, and have been

<sup>1</sup> *Bull. de la Soc. de l'Industrie Min.*, 1888, p. 505.

<sup>2</sup> Massart, *loc. cit.*

to a great extent replaced by the latter. The larger furnaces, fired by gas, should therefore be preferred as a rule to the smaller grate-fired furnaces. (Firket, *op. cit.*) The efficiency of the older Belgian furnaces in use in England has already been given. The Ferraris furnace at Monteponi has 180 retorts, in which 6 to 7 tons of calcined calamine are worked off in 24 hours.<sup>1</sup>

The zinc works in the Eastern States of North America (Bergen Port, Passaic Works, Newark and Bethlehem) employ Belgian furnaces with Wetherill grates burning anthracite.<sup>2</sup> The following is an account of the process as practised there towards the end of the seventies. At the Bergen Port Zinc Works, New Jersey, where calcined blende containing 26 per cent. of oxide of iron was treated, the furnace contained 70 retorts. Each furnace could put through 3,175 lb. of calcined blende with 1,900 lb. of anthracite for reduction, in 24 hours, with a consumption of  $2\frac{1}{2}$  tons of anthracite for fuel. The loss of zinc varied from 24 to 26 per cent. The two topmost tiers of retorts were only charged once in 24 hours, the five lower tiers twice. The condensed zinc was removed six times in 24 hours from the adapters. The consumption of coal per ton of zinc amounted to 5.5 tons for heating and 1.9 for reduction, or altogether 7.4 tons. Every 24 hours five retorts were destroyed per furnace, or 7.1 per cent. The reason of the comparatively great consumption of fuel and of retorts, together with the high loss of zinc, was caused by the large percentage of iron in the charge. The furnace campaigns lasted about a year.

At the Passaic Zinc Works, in Jersey City, the furnaces also contained 70 retorts each. The charge for the furnace consisted of 27 cwts. of a mixture of willemite and calamine. The three lower rows were charged twice in 24 hours, the remaining ones only once. In 24 hours 10 cwts. of zinc were produced, with a consumption of  $2\frac{1}{4}$  tons of coal for fuel. The extraction of zinc amounted to 80 per cent. of the contents of the ore. One ton of zinc required 4.5 tons of coal for fuel and 1.3 tons for reduction, or a total of 5.8 tons. In 24 hours 6.4 per cent. of the number of retorts in the furnace was destroyed. A furnace campaign lasted two years. The furnaces at present contain 216 to 252 retorts.<sup>3</sup>

At the Lehigh Zinc Works, near Bethlehem, Pennsylvania, the furnaces contained 56 retorts, and held a charge of one ton of ore, consisting of a mixture of calamine and blende. The topmost row of

<sup>1</sup> *The Mineral Industry*, 1902, p. 670.

<sup>2</sup> Strecker, *Jahrb. d. K. K. Bergak.*, 1879, p. 282.

<sup>3</sup> Ingalls, *op. cit.* p. 656.

retorts, containing zinc fume and skimmings, was only charged once in 24 hours, the six lower rows twice. For one ton of ore 1·8 tons of coal were consumed as fuel. The production of zinc amounted to 73·5 per cent. For each ton of zinc 4·5 tons of coal as fuel and 1·7 tons of coal for reduction, or a total of 6·2 tons of coal, were required. 3·7 per cent. of retorts were destroyed daily. The furnace campaigns lasted for 15 months.<sup>1</sup> The yield of zinc was 82 per cent.

At the Bertha Works, near Pulaski in the State of Virginia, which produce zinc well known for its purity and freedom from lead (Zn 99·981 per cent., Fe 0·019 per cent.), the ore treated being calamine free from lead, there are 10 modified Belgian furnaces fired by grates, each of which contains 140 retorts, of oval cross-section having a length of 4 feet, the larger diameter being 10 inches and the smaller being 8 inches in the clear. Long-flamed Pocahontas coal is used as fuel, anthracitic coal for the purpose of reduction. The charge of a furnace consists of 4·25 tons of calcined ore and 3 tons of coal. The distillation occupies 24 hours, the output of zinc being 80 per cent. Five men work a furnace in 24-hour shifts.

At the works of the Matthiesen and Hegeler manufacturing Company at La Salle,<sup>3</sup> there were towards the end of the seventies two forms of gas-fired furnaces, namely, small double furnaces with 136 retorts, and a large double furnace with 408 retorts. The producers were provided with oblique grates built of fire-brick. The bricks were supported upon cast-iron bearers, the necessary space for the admission of air being left between them. This arrangement is necessitated by the fact that the only available coal is very apt to clinker. There were five tiers of retorts in all the furnaces. The uppermost row consisted of the retorts with rectangular cross-section described on page 151, which take a charge two or three times as great as that of the regular retorts. The furnaces were divided into sections which contain 4 tiers of 7 cylindrical retorts and 1 row of 6 prismatic retorts each. The smaller furnaces have two of these divisions on either side, the larger six; the topmost row against which the flame strikes was first charged with blende, the second and third with calamine, and the lowest with zinc fume and residues rich in zinc. The output of the large double furnaces amounted to 5 to 6 tons of zinc per 24 hours. The loss of zinc was 18 per cent.; the destruction of retorts amounted to 25 per cent. At present the largest double furnaces contain 448, 864, and 1008 retorts.<sup>4</sup>

The gas-fired furnaces of the Missouri Zinc Company, in St.

<sup>1</sup> Ingalls, *loc. cit.*

<sup>2</sup> *Eng. and Min. Journ.* 1893, vol. lvi, No. 22.

<sup>3</sup> Strecker, *loc. cit.*

<sup>4</sup> Ingalls, *op. cit.*

Louis,<sup>1</sup> contain 160 retorts each. They are charged with calcined silicate of zinc, the weight of which in the raw state amounts to  $4\frac{1}{2}$  tons. The amount of coal employed for the reduction of this charge is 31·5 cwt., 8 tons of coal being consumed as fuel. The output of zinc is equal to 70·71 per cent. For each ton of zinc 4·4 tons of coal are used as fuel. The destruction of retorts is considerably less than it is in direct-fired furnaces. The Jola furnaces, which are fired with natural gas, contain 600 to 660 retorts, put through 10·8 to 11·8 tons of ore, mixed with 40 to 50 per cent. of coke and lean coal, in 24 hours.<sup>2</sup>

## II.—ZINC DISTILLATION IN MUFFLES, OR THE SILESIA PROCESS

This form of distillation, as already stated, is carried out in reverberatory furnaces in which muffles are arranged. The gaseous zinc thus produced is condensed in adapters of various forms attached to the muffles.

### *Muffles*

The muffles, as previously stated, generally assume the shape of prismatic boxes, with an arched top. In some instances they consist of oblong boxes flat on top, with rounded edges. The rear side is closed whilst the front remains open. During the distillation the lower half of the latter is closed by means of a fireclay slab, whilst the upper portion is closed by the end of the adapter, which is luted on tightly with clay. The front end of the adapter rests upon a step supported on either side by projections from the longer walls of the muffle. If the front end of the adapter is tube-shaped, the upper half of the muffle must be closed by means of a slab of clay, provided with a short cylinder into which the end of the adapter fits. The front end of the muffle and the upper plate with its short cylinder are shown in Figs. 137 to 139. As has been stated above, the muffles are generally 26 inches high in the clear, 6 to 8 inches wide, and 28 inches to 7 feet long. If the entire bottom of the muffle is supported, its length may be as much as 7 feet. If, however, it is

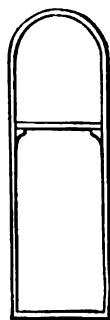


FIG. 137.



FIG. 138.



FIG. 139.

<sup>1</sup> Strecker, *loc. cit.*

<sup>2</sup> Ingalls, *op. cit.* p. 652.

only supported at the front and back ends, its length must not exceed 4 feet. The bottom and sides of the larger muffles are made thicker at the back than in front. In Upper Silesia, for instance,<sup>1</sup> the thickness of the walls increase from the front to the rear portion of the muffle from 0·8 to 1·2 inches in the arch, and the thickness of the bottom from 0·8 to 2·5 inches. The material from which the muffles are manufactured is a mixture of raw and burnt clay, the latter of which may be replaced in part by fragments of muffles. The composition of suitable varieties of clay has already been given on page 115.

In Upper Silesia, where only big muffles are employed, these are made by hand. Where small muffles only are in use, as in distillation in Rhenish-Westphalian furnaces, machinery is used for their manufacture. When made by hand, muffles are made either vertically or horizontally. When vertical muffle moulds are employed, the latter generally consist of three sections fastened together by means of hooks and eye bolts. As in the manufacture of retorts, the back portion of the muffle is first shaped in the bottom portion of the mould, the second section is then attached to the first and the middle of the muffle is shaped in it, and then the front section is attached to the former portion and the rest of the muffle moulded in it. Finally, the projections to carry the step at the front portion of the muffle are attached. The various slabs of clay are fastened to each other, as in the case of the retorts, by scoring the portions in contact by means of a small comb. When the muffles are made horizontally, as in Upper Silesia,<sup>2</sup> the bottom is first made by cutting out a hollow in a prismatic piece of clay of the size of the bottom of the muffle, which is then placed in the lower portion of the muffle mould. Slabs of clay of the height of a segment of the mould are then introduced and united, the diagonally cut end of the slab being scored, moistened with water, and then pressed against the correspondingly cut end of the next piece. The slabs of clay are then pressed against the corresponding portion of the mould and beaten down with an iron beater. This process is continued until the muffle is complete. Generally four or five muffles are commenced simultaneously; the advantage obtained thereby is that when the work is completed the muffle is already dry enough to admit of the mould being removed.

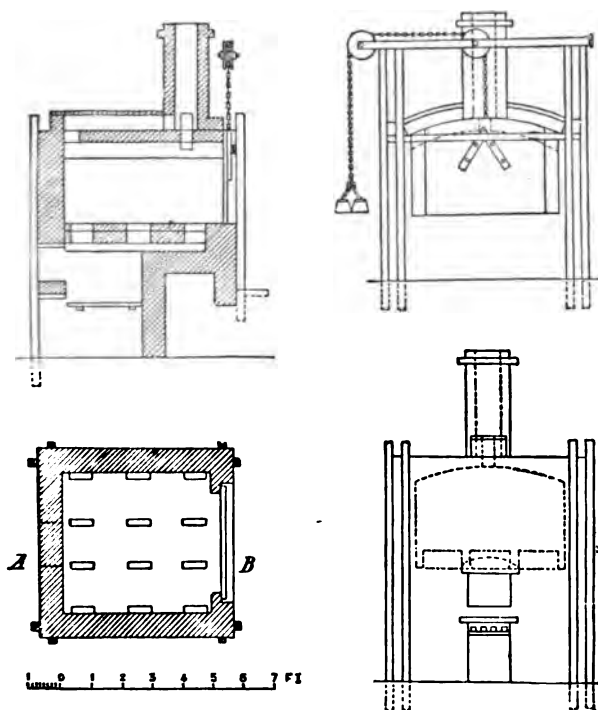
Wernicke prepares muffles with the bottom uppermost, by beating the clay between the bottom and the core. This method has, however, not found extensive application, since by the use of better materials, muffles are now made with thinner walls than formerly,

<sup>1</sup> Georgi, *Berg- und Hüttenm. Ztg.* 1877, p. 72.

<sup>2</sup> Georgi, *loc. cit.*

and beating is unsuitable for the production of the walls. Although it has been proposed to manufacture Silesian crucibles by machinery,<sup>1</sup> yet this method has not been persisted in, as such muffles have not proved satisfactory. No reasons have been given for this. The muffles are dried standing on end for a certain time, up to one month, in drying chambers heated to between 30° and 33° C., then glazed if desired, and finally kept until required for use (up to a period of 12 months) in drying chambers at a temperature of 35° C.

Muffles must be introduced red-hot into the furnace. They are therefore previously heated, 12 to 14 hours, by the waste heat



FIGS. 140-143.

of the distillation furnace, or in special reverberatory kilns provided with grate fires. The construction of such a furnace is shown in Figs. 140 to 143. Above the grate there is an arch pierced with twelve openings, through which the flame enters the heating chamber; the latter is provided with a door lined with firebrick, which can be raised or lowered by means of counterpoises. At the Paul Works, near Rosdzin, in Upper Silesia, such a furnace takes 12

<sup>1</sup> Steger, *Preuss. Zeits. für Berg- und Hüttenm. u. Salinenwesen*, 1900, p. 419.

to 14 muffles at a time. Their heating or annealing lasts 12 hours, 5 cwts. of coals being consumed. A muffle lasts 30 to 40 days.

### *Condensers or Adapters*

These are of various shapes. In the older Silesian furnaces they consisted of a bent clay pipe composed of several pieces which communicated with a chamber in which the zinc, condensed in the pipe, accumulated. In the newer furnaces they are given the form of cylindrical tubes, or of cylindrical tubes bellied below, or of prismatic boxes with an arched top. The arrangement of the adapter for the old Silesian furnace, which is now no longer employed, is shown in

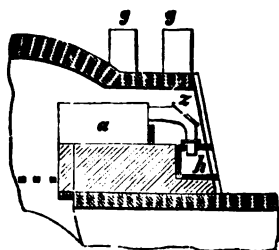


FIG. 144.

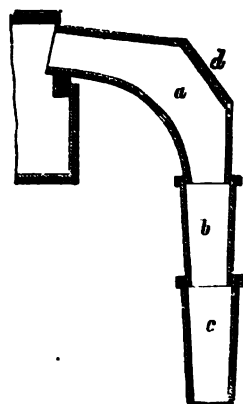
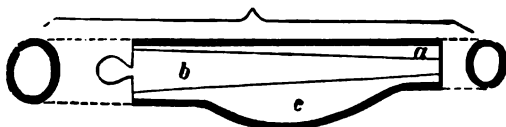


FIG. 145.

Figs. 144 and 145. In the former, *h* is the chamber in which the fluid zinc solidifies; in the latter figure *a* is the upper portion of the adapter made of clay, which rests upon the step of the muffle. It has an aperture at *d* which can be closed by a tile; the muffle can be charged through this aperture by removing the latter; *b* is a tube made of cast-iron, *c* one of sheet-iron, the latter entering into the collecting chamber. The zinc condenses in the knee-shaped tube, and flows through the vertical portion into the chamber. The employment of this adapter makes it necessary to re-melt the solidified zinc, in order to cast it into moulds. As above mentioned, it has been replaced by other forms of adapters. Adapters which have the shape of tubes bellied underneath are shown in Figs. 146 and 147. The fluid zinc collects in the bellied portion and is raked out from it from time to time; a sheet-iron cone or nozzle is attached to its front



end. Inclined cylindrical tubes, as shown in Fig. 148, are also used as adapters. In this case their front end is closed with a tile, or with an iron plate clayed over, and having a hole through the centre. The zinc that collects in this adapter is allowed to run into an iron ladle held in front of it, by removing or loosening the plate; for this purpose the clay luting which connects the lower portion of the



FIGS. 146 and 147.

plate to the adapter is gradually loosened. The same method of closing is used for adapters made in the shape of prismatic boxes. The gases escape through a short tube projecting from the front slab into a nozzle. In order to condense the zinc vapours more completely, to collect zinc fume, and to avoid the injurious effects of the gases and vapours escaping from the adapters, these have received important improvements in recent times in Upper Silesia. Of these new adapters, the most important are those of Kleemann and of Dagner.

The Kleemann adapter is shown in Fig. 149,<sup>1</sup> and has the shape of an inclined cylinder, or of a parallelepipedon, or of a prismatic



FIG. 148.

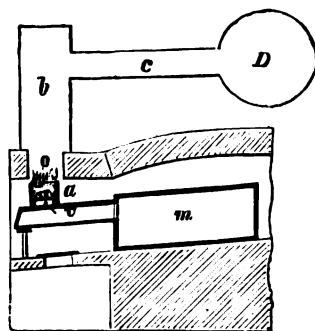


FIG. 149.

box with arched roof 3 feet 3 inches long, to the front portion of the roof of which a flange 4 inches high is attached. Above this is a cast-iron grating upon which a layer of coke is maintained at a red heat. The back portion of the adapter is secured to the muffle; the front open portion is closed with an iron plate covered with clay

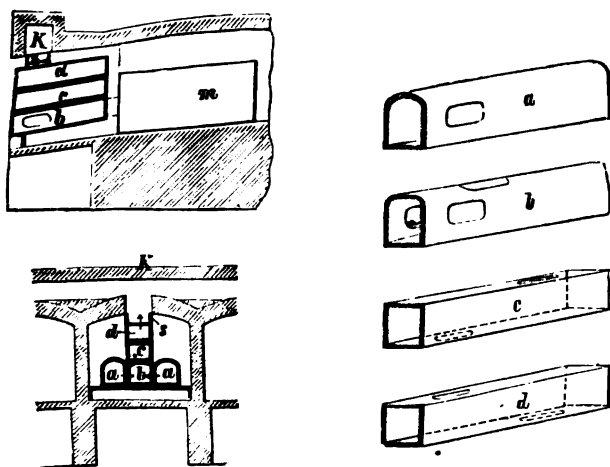
<sup>1</sup> D. R.-P. Nos. 8121, 12821, 28596; additional Patent, 7411.

and luted as tightly as possible to the adapter. There is an opening in the centre of the plate, which can be kept closed by means of a clay plug. The whole adapter lies inside the recess of the furnace. The gases, consisting mainly of carbon monoxide and of the metallic particles which are not deposited in the receiver, are forced to pass through the grating and the layer of glowing coal. A portion of the metallic constituents of the vapour is retained in the layer of coke, whilst the carbonic oxide is heated to the point of combustion, and is burnt by a current of air. Any zinc oxide contained in the gases is not reduced by the bed of coke. As the layer of coke soon becomes stopped up, it requires frequent stirring, and must be renewed from time to time. In consequence of the layer of glowing fuel upon the grate, no oxygen from the air can enter the adapter. The burnt gases and the metallic particles not retained in the bed of coke pass through an opening in the arch of the recess into a flue running above the furnace, or into a main flue, whence they are conducted into an apparatus for the precipitation of the metallic particles, and finally escape into the stack. In the above figures the burnt gases escape from the adapter *v*, through the grating at *a*, by the opening *o* and the flues *b* and *c*, into the main flue *D*, and from the latter into the stack. The zinc is tapped out from the bottom end of the adapter. These adapters are at present in use at the Silesian Works, near Lipine. The gases and vapours escape through the layer of burning fuel into a main longitudinal flue, thence into an underground dust chamber, and finally to the stack. No deposit of oxides may show upon the coping of the stack, as this would be a sign that the flue dust has not been completely collected. There is a small sight-hole at the front of the adapter, which can be kept closed by clay. If any flame escapes from this sight-hole, it shows that the passage of the vapours through the layer of fuel has been hindered by the deposition of particles of metal and oxides in the latter, which obstacles must then be removed or the bed of fuel be renewed. This adapter, which has rendered good service at the Silesian Works, has been replaced in many works by the Dagner adapter.

The Dagner adapter<sup>1</sup> serves to condense the zinc vapours from a pair of adjacent muffles, and consists of a series of inclined boxes which lie beside or above each other, in which the greater portion of the metallic constituents of the vapour is deposited. The arrangement of the adapter is shown in Figs. 150 to 155; in these *a*, *a* are the two adapters fitted to the pair of muffles *m*, lying side by side.

<sup>1</sup> D. R.-P. No. 8958.

The gases and zinc vapours escape from lateral openings in these adapters into a chamber *b* lying between them. Through an opening in the upper part of the latter they escape into a prismatic box *c*, 24 inches long, traverse this lengthways, and then rise up into another prismatic box *d* of the same length, which they also traverse longitudinally, and then escape through an opening provided with a short branch into the flue *K*. When they escape through the top-most box, these gases are burnt by a current of air, so that their products of combustion, together with any zinc vapours that have escaped combustion, enter the flue *K*. The front ends of these adapters are closed by plates of sheet iron, which are covered with



FIGS. 150—155.

clay on either side, and are luted to the adapters. In the middle of each plate there is a small round hole, which can be closed at will by a clay plug. Through these holes iron rods can be introduced into each separate portion of the adapters in order to remove deposits of zinc oxide from within them. The separate recesses are closed in front by plates of sheet-iron.

The zinc collects in the lower adapter in the fluid condition; in the upper adapters zinc oxide and zinc fume are deposited. The zinc is tapped off from the front end of the adapters. From the other adapters the zinc fume and oxide are raked out after the front plates have been removed. On account of the long distance which the gases have to traverse through these adapters and boxes, the greater portion of their metallic constituents is deposited. The remainder, together with any zinc oxide formed by the combustion of

zinc vapours at the outlet, passes into dust chambers connected with the adapters. The division *b* of the adapter is 6 inches broad and 8 inches high; the division *c* is  $4\frac{1}{2}$  inches broad and 4 inches high; the division *d* is 10 inches broad and 10 inches high. The burnt gases and vapours after passing through the main flues, dust chambers, and dust towers, finally pass into a flue with a powerful draught. At the Paul and Wilhelmina Works, near Schoppinitz, the gases escape through horizontal pipes. The recess is here closed in front by a temporary wall, in the lower portion of which there is a small opening. Through the latter the air required for burning the gases enters the recess and directs the flame towards the collecting flues. Through these flues the gases pass into a system of condensing chambers. These chambers, of which there are 7, having a total length of 360 feet, are provided with vertical walls, by which the distance to be traversed by the current is prolonged and the surface exposed to it increased. In the last chamber any remaining solid particles, carried by the current of gas, are removed by means of a water spray, after which the gases escape into the stack. The water flowing through this last chamber is run on to a coke filter, which retains the solid particles, the water running clear from the last filter. This arrangement has given satisfactory results. The composition of the zinc fume collected in the condensing chambers of the Wilhelmina Works when the Dagner adapter is used is the following:—

ZnO . . . . .	88.20 per cent.
CdO . . . . .	1.46 „
PbO . . . . .	4.44 „
SO <sub>3</sub> . . . . .	4.12 „
Mn <sub>3</sub> O <sub>4</sub> . . . . .	0.05 „
Fe <sub>2</sub> O <sub>3</sub> and residue . . . . .	1.50 „
	<hr/>
	99.77 „

Adapters are composed of ordinary potter's clay with the addition of a certain quantity of burnt clay or of fragments of muffles, or at times of the distillation residues from the zinc retorts, or of coke dust. They are made by hand, slabs of clay of the requisite length being laid upon wooden cores of the shape of the adapter, and pressed down upon them. As soon as the mass has attained a sufficient degree of consistency, the core is withdrawn. When a bellied adapter has to be made, as is shown in Fig. 146, the core consists of three pieces, *a*, *b* and *c*, the middle wedge-shaped portion of which,

*b*, is provided with a handle, so that it can be drawn out. The slab of clay is laid upon the core and beaten down by hand. As soon as it has attained a sufficient consistency, the wedge-shaped portion of the core is withdrawn; the portion *a* then drops down, and can be drawn out, and the portion *c* is lastly lifted out from the adapter. These adapters are either dried upon the roof of the distillation furnace and used raw, or else are burnt after having been dried by

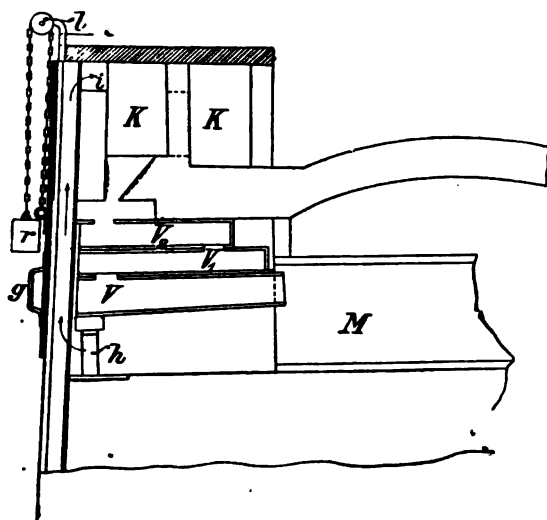


FIG. 156.

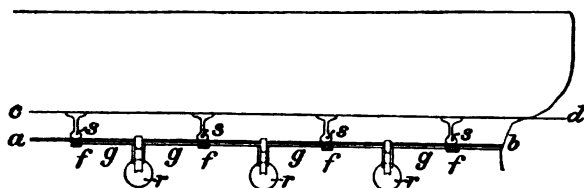


FIG. 157.

the waste heat of the distillation furnace, or in special annealing kilns. Adapters last from 2 to 3 weeks.

In order to protect the workmen against the gases and vapours which escape when the muffles are being cleared out and charged, and also against the zinc vapours which escape during distillation, through the sight-holes and through cracks in the adapters, an arrangement has been introduced by Stempelmann at the Hohenhe Works, near Kattowitz, with good results. It is, therefore, combined with the Dagner adapter, the arrangement being shown

in Figs. 156 to 158.<sup>1</sup> Above the uppermost adapter a sheet-iron plate *a b* is so secured to the buckstaves of the furnace as to form a flue, the walls of which consist of the above sheet-iron, the true furnace wall *c d*, and of a pair of buckstaves *s*. At the upper end there is a lateral aperture *i* through which the gases and vapours ascending can escape into the dust chamber *K*. This flue can be prolonged downwards by means of a sliding sheet of iron provided with a handle and suspended by means of a chain with a counterpoise. It is guided by means of iron castings *f* riveted to the sheet-iron *a b*. When the muffle is to be cleared out, the sliding sheet is lowered so far that the gases and vapours escaping from the former rise through the opening *h* into the prolongation of the flue,

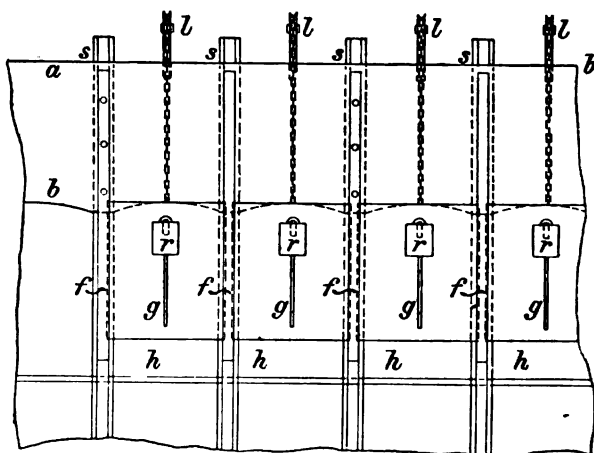


FIG. 158.

and thence escape through the opening *i* into the dust chamber *K*. When the muffle is being charged, the sheet-iron must be lifted up so far that the front end of the adapter *V*, through which charging takes place, stands open. The gases and vapours then also escape into the above-named flue, and find their way through *i* into the dust-chamber.

Wherever the adapters of Kleemann and Dagner are not in use, nozzles or condensers of sheet-iron are often attached to the front end of the adapters in order to collect the metallic portion of the vapours and to prevent injury by the escaping gases. The metallic portion of the vapours condense and thus form a mixture of pulverulent zinc and zinc oxide, known as zinc fume or "*poussière*." These nozzles may communicate with draught flues to remove the poisonous

<sup>1</sup> Saeger, *Hygiene der Hüttenarbeiter*, Jena, 1895.

carbonic oxide; otherwise this gas escapes through the front end of the former. Such nozzles are at present universally used for Belgian and Belgo-Silesian furnaces. The most improved forms of these, formerly used in Upper Silesia, and still at present used to some extent, are the twin cylindrical nozzles of Recha, the cylinder of Bugdoll, the vertical nozzle with condensing chamber, and the appliances devised by Palm, by Hawel, by Mielchen, and by Steger.

Fig. 159 shows Recha's nozzle. It consists of 2 cylinders of sheet-iron *A* and *B*, connected with each other. The sight-hole of the

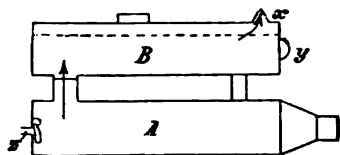


FIG. 159.



FIG. 160.

cylinder *A* is closed by an automatic valve *z*; the cylinder *B* has a cap *y*. The gases which are not combustible escape through the latter cylinder by means of the tube *x*, and can be conducted away by means of a hood attached to the front side of the furnace into the flues or above the level of the furnace top.<sup>1</sup>

Fig. 160 shows the nozzle of Bugdoll.<sup>2</sup> It consists of a cylinder closed in front; by means of a valve *b* the particles of fumes deposited in the cylinder can be removed. The gases and vapours escape through the branch *v*; the latter is closed by a gas filter of fine cotton in which all solid parts of the gases and vapours are retained.

Fig. 161 shows the vertical nozzle with condensing chamber; *b* is the vertical nozzle connected on one side with the adapter *v* by

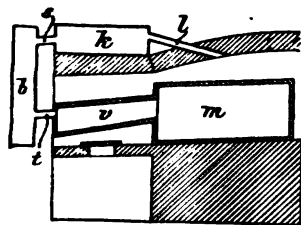


FIG. 161.

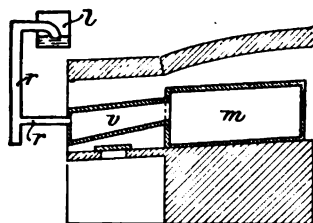


FIG. 162.

means of the tube *t*, on the other side with the condensing chamber by means of the tube *s*. Through the latter, gases and vapours that have not been condensed escape by the tube *l* into the interior of the distillation furnace, where they are burnt. By means of two

<sup>1</sup> D. R.-P. No. 12768.

<sup>2</sup> D. R.-P. No. 11545.

apertures provided with sliding covers the nozzle *b* can be cleaned out.

The apparatus of Palm<sup>1</sup> is shown in Fig. 162; the gases and vapours escaping through the adapter *v* pass through the tube system *r r*, into the collecting tank *l*, filled with water, and in escaping, impinge upon the surface of the water. From this tank they pass through several other washing tanks, and then escape into the fireplace of the furnace.

In Hawel's arrangement, shown in Fig. 163,<sup>2</sup> a chamber *k* is provided over every pair of adapters, the former being connected with a gas delivery tube *n*. The nozzle is connected both with the chamber

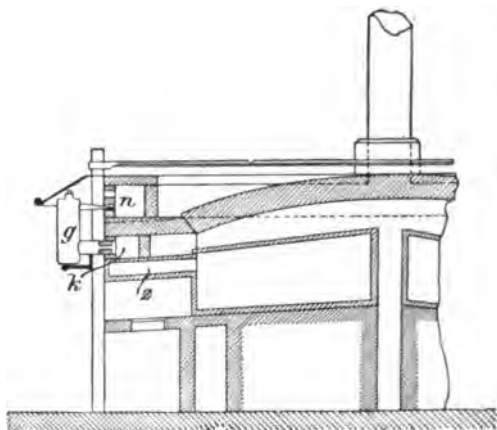


FIG. 163

and with the gas tube by means of short pipes. The vapours pass first into the chamber, then into the nozzle, and finally into the gas flue. The greater portion of the zinc escaping through the adapter is condensed in the chamber *k*, and flows back into the adapter : over the inclined floor of the former. By means of a pipe recently placed by Hawel between the adapter and the chamber, better results have been obtained as regards the condensation of zinc vapours.

The nozzle of Mielchen<sup>3</sup> used at the Hugo Works, in Upper Silesia, is shown in Figs. 164 to 166.<sup>4</sup> There are two adapters *d*. Fig. 166, from which the gases and vapours escape through two tubes of sheet-iron *c* into a sheet-iron cylinder *e*, provided with hand holes *f*, and pass by means of the perforated sheets *g* into the tube

<sup>1</sup> D. R.-P. No. 9672.

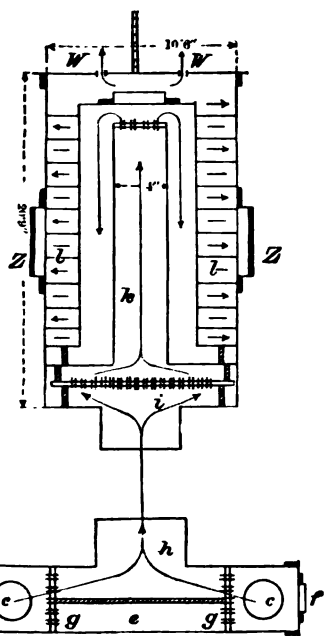
<sup>2</sup> D. R.-P. No. 18635.

<sup>3</sup> D. R.-P. Nos. 57385 and 61740.

<sup>4</sup> Saeger, *op. cit.*



*h*, upon which the nozzle proper is supported. The latter consists of an inner cylinder of sheet-iron *k*, resting upon a perforated iron plate *i*, the upper end being also perforated, and of an iron cylinder *l* which slips over the former, and which is in its turn surrounded with 9 spiral rings made of sheet-iron, which are tightly riveted to the outer wall. The gases and vapours escape through the perforated cover of the inner cylinder into the annular aperture between the inner and the outer one, through the lower end of this space pass at the lower end of the latter into the space between the inner cylinder and



FIGS. 164 and 165.

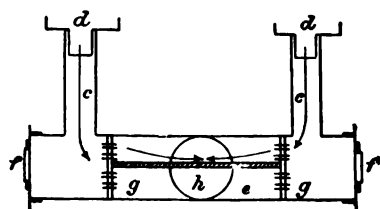


FIG. 166.

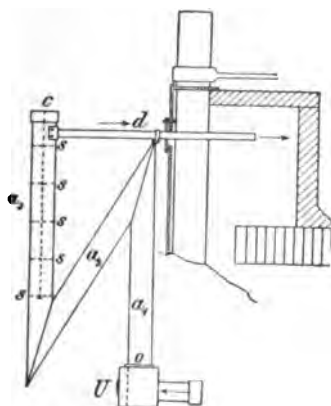


FIG. 167.

the nozzle, and then take the spiral route indicated by the arrows, escaping finally through the openings *W* in the cover of the nozzle; the apparatus is provided with the handles *Z*. On account of the long route traversed around the outer cylinder, the deposition of the metallic portions of the gases is almost complete. This nozzle requires most careful attention.

Steger's nozzle, which is used at the Lazy Works, near Beuthen, is shown in Fig. 167. The gases and vapours escape from the adapter, first into the lower cylinder *U*, then traverse the sheet-iron tubes *a*<sub>1</sub>, *a*<sub>2</sub>, and *a*<sub>3</sub>, which form the nozzle proper, and escape at

the upper end of the latter through the tube  $d$  into a flue, in which they are burnt and led away. In the tube  $a_3$  discs of iron are arranged, by which the gases are forced to ascend close to the outside circumference of the tube. The zigzag arrangement of the tubes forces the gases to traverse a considerable distance, and at the same time alters their direction repeatedly. The gas is also exposed to the contact of a very extensive surface, and is thus greatly cooled on account of the material of which the tubes consist. The cooling effect is increased by the action of the discs  $s$ , which force the gas current against the wall of the tube  $a_3$ . In consequence of these arrangements, the current of gas is cooled far below its temperature of ignition, so that even should air find its way into the nozzles, explosions are not to be feared. It is said that the amount of zinc fume obtained in this nozzle is very considerable, and greatly exceeds that obtained in the others.

#### *Furnaces for Distillation*

In the old Silesian furnaces with grates the flame rose up, surrounded the muffles laterally, and then escaped, partly through openings in the arch of the furnace, partly through lateral apertures. In the newer furnaces fired by grates or fired by gas, the flame rises up to the arch and then returns, surrounding and striking the muffles from above, and escaping at the bottom of the furnaces. The furnaces of the latter type have been called Belgo-Silesian furnaces. As, however, this name has been applied to furnaces with several horizontal tiers of muffles, some confusion has arisen. To obviate this, furnaces of all kinds with a single row of muffles will be called Silesian furnaces; those with more than one row of muffles Belgo-Silesian furnaces. The old Silesian furnaces were formerly used universally in Upper Silesia, the short-flaming coal which is there obtainable being the fuel employed. At present, however, they have everywhere been displaced by the Belgo-Silesian furnaces. The latter, which are suited for coals giving long flames, and for various forms of gas-firing, economise heat to a far greater extent than do the old Silesian furnaces, which nowadays scarcely possess more than historical value.

#### *Old Silesian Furnaces*

These are furnaces with a long narrow fire-chamber. In their longitudinal axis a deep grate is built, upon either long side of which

the muffles rest upon supports. The flame rising from the grate surrounds the muffles laterally, and then escapes partly through lateral openings in the short side of the furnace into the chambers for calcining calamine, for annealing muffles, and for re-melting the zinc, and partly escapes through a row of flues in the arch of the furnace, either into a main flue leading into a large stack or directly into low stacks. The arrangement of such a furnace is shown in Figs. 168 to 170, in which *b* is the grate; its length is 5 feet 5 inches,

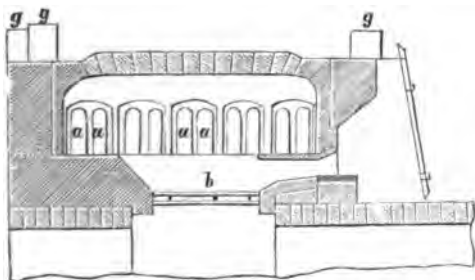


FIG. 168.

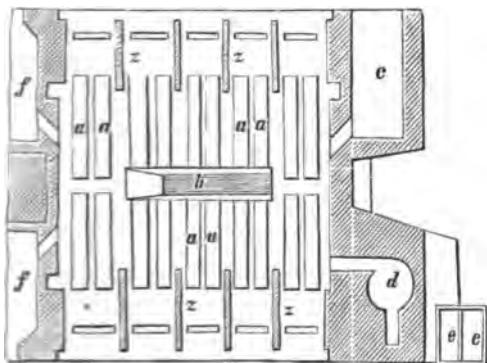


FIG. 169.

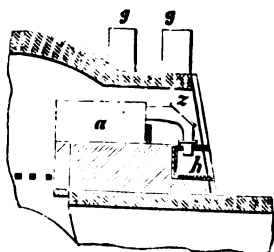


FIG. 170.

and its depth 2 feet 6 inches below the floor of the furnace. It is fired by means of a fire door shown in Fig. 168. Along the two long sides of the grate, or upon their prolongation, 10 muffles are arranged. The roof of the furnace is built of fireclay or of fire-bricks. Each pair of muffles opens in front into recesses 29 inches high and 26 inches wide, which are known as *chapels*, these being separated from each other by partition walls, *Z*, 4 feet 4 inches long and 4 inches thick. The adapters of the muffles lie in these recesses. These furnaces, each of which holds 20 muffles, are built in pairs. After

the flame has heated the muffles from the side, it escapes through lateral openings in the shorter walls of the furnace, partly into chambers for calcining calamine, partly into chambers for annealing muffles and for re-melting the zinc, and then from these into low stacks; *f, f* are the calcining chambers built between a pair of neighbouring furnaces, *e* is the chamber for annealing the muffles, and *d* the chamber for re-melting the zinc; *h* is the chamber into which the adapter opens, and in which the zinc collects in the solid form. The front part of this chamber is closed by means of a door during the course of the operation; *g, g* are the stacks. The bottoms of the muffles in the case of these furnaces rest upon a solid support, and are, therefore, not struck by the flame.

Furnaces of this kind have been used in England and fired by means of highly bituminous coals. In the arch over the front portion of the muffles there are two rows of holes, whence the products of combustion escape into horizontal flues leading to the stack, no attempt being made to heat annealing or calcining chambers. Each furnace contains 24 muffles. On account of the inefficient utilisation of the heat in these furnaces, 1 part by weight of zinc required for its reduction, from comparatively poor ores, 17 to 20 parts by weight of coal in Upper Silesia; with richer ores and better coals in England  $11\frac{1}{2}$  parts of coal. The loss of zinc in Upper Silesia was as high as 30 per cent., and in England amounted to 18 per cent. As already stated, these furnaces have been replaced by the new Silesian furnaces, and are now no longer built.

#### *New Silesian Furnaces*

These furnaces have been evolved from the old Silesian furnaces, the flames not being allowed to escape from the furnace either laterally or through the arch, but being first made to strike the arch and then to return, escaping at the bottom of the furnace. Thus the products of combustion escape either through a common flue running under the bottom of the furnace into a stack, or into several stacks, or before entering the latter they can be utilised for calcining calamine. By this means heat has been more effectually utilised (6 to 8 parts of coal to 1 part of zinc), the temperature is kept more uniform, the retorts last for a longer time, the output of zinc is greater, and the furnaces can be adapted for a larger number of muffles, and their capacity thereby increased. It was also found possible to avoid the entrance of smoke into the works, and to minimise the injury done by the smoke to the surrounding country.

This method of heating was first introduced at the works of the Vieille Montagne Company in Belgium and Westphalia, flat grates and highly bituminous coals being employed; this is the reason why these furnaces have received the name of Belgo-Silesian furnaces. In the case of the less bituminous coals of Upper Silesia ordinary grates could only be employed, when the layer of fuel was raised up to a considerable height by a bed of clinker, an air blast being forced into the ashpit under the grate, or above the grate at the level of the top layer of fuel. A further improvement was the introduction of gas-firing, which considerably increased the capacity of the furnaces, and has almost completely displaced fire grates. As a rule, therefore, gas-firing should at present be exclusively used for Belgo-Silesian furnaces. The number of muffles in the newer furnaces of this class is from 24 to 80; two furnaces are generally combined to form a block. It is best to separate the above classes of furnaces into furnaces fired by grates and those fired wholly or in part by gas. Furnaces fired by gas may be divided into furnaces without and with regenerators.

#### *New Silesian Furnaces Fired by Grates*

Furnaces of this kind were frequently used before the introduction of gas-firing, but have been replaced by gas-fired furnaces at most works. The construction of such a furnace with one row of muffles, as used at Valentin-Cocq, in Belgium, is shown in Figs. 171 to 175. There are 16 muffles *c* on either side of the grate. Two such furnaces are built together, being united by their shorter sides. The flame rising through the grate ascends to the arch and then descends, enveloping the muffles from above and escaping through a row of apertures into the flues *k* in the floor, which lead the products of combustion to the stack. In the older furnaces there are calamine calcining chambers, *Z*, between each pair, or whenever solid zinc was produced, as in the old Silesian furnaces, chambers for re-melting the zinc, *a*, were also provided. In either case a portion of the flame was diverted through these chambers before entering the stack; *v* are vertical shafts, through which the distillation residues that remain in the muffles are dropped into horizontal arched tunnels *T*. The latter open into a tunnel, *w*, running parallel to the longitudinal axis of the furnace; *u* are the adapters already described for the collection of the zinc, *q* the nozzles attached to them for collecting zinc fume. The adapters are arranged in recesses, which have already been

considered under the heading of the old Silesian furnaces; *t* are the steps at the front end of the muffles, upon which the rear end of the adapter is supported. The front end of the latter rests in an iron frame which closes the front of the recess. The upper portion can

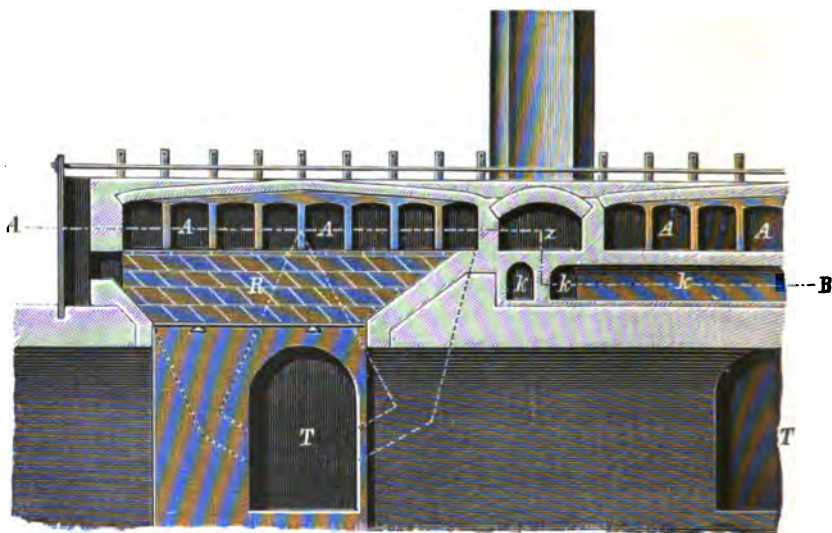


FIG. 171.

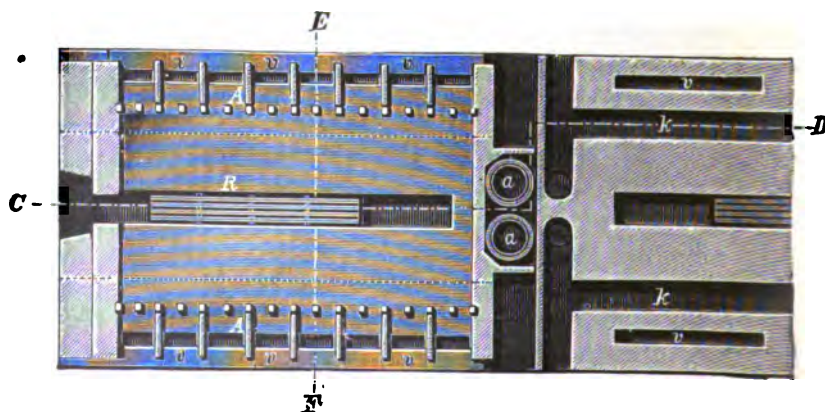


FIG. 172.

thus be closed, the lower portion being fitted with a tightly shutting door. This form of adapter through which the zinc has to be raked out is often replaced by one or other of the above-described adapters, from which the zinc is tapped out.

On account of the small, non-bituminous coal available in Upper

Silesia, it was necessary to employ clinker grates with a blast underneath them, or in some cases to use a blast above the top of the fuel. Furnaces of this kind hold from 24 to 28 muffles. The clinker grate is kept 10 inches in height, the blast being produced by means of fans or injectors and conveyed by means of a pipe into the closed ashpit of the grate. When a top blast was used, it was first heated by circulating through flues in the brickwork of the furnace, and then

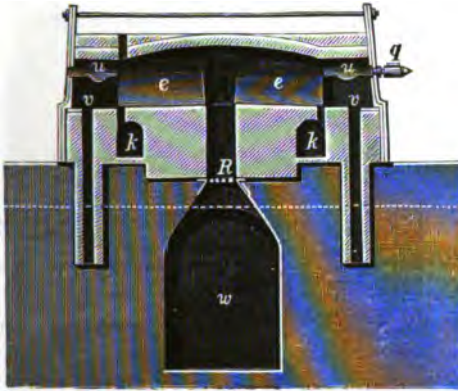
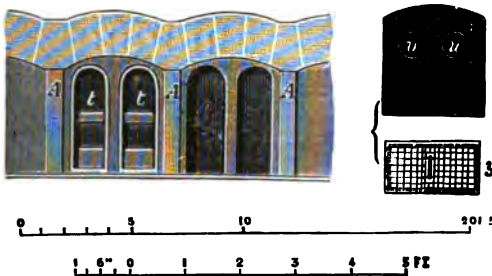


FIG. 173.



FIGS. 174 and 175.

entered the grate by means of small apertures. Furnaces of this kind have been replaced in the Upper Silesian works by gas-fired furnaces.

#### *New Silesian Furnaces Fired by Gas*

Gas-fired furnaces admit of the employment of inferior fuel and the production of a high degree of temperature, equable heating of a large furnace, and of convenient stoking of the gas producers. On this account the capacity of gas-fired furnaces is considerably greater

than that of furnaces fired by grates. They should, therefore, be used as a rule. The products of combustion either pass directly into the flues or a portion of their heat may first be utilised for calcining calamine and for annealing muffles, or for heating regenerators. Regenerators of the Siemens type are employed. The latter imply, however, a high first cost, careful attendance, and a uniform and not too inferior quality of coal. There is also danger of the flues of the regenerators becoming readily stopped up by zinc oxide and by the carbonaceous matter deposited by the tar, so that in spite of the great advantages of the Siemens furnace it has not found the universal application in zinc works that was expected from it.

### *Gas Furnaces without Regenerators*

When gas furnaces are employed without regenerators, the air necessary for the combustion of the gases is heated either by passing through flues in the brickwork of the furnace or of the gas producer, or in flues which are surrounded by the escaping products of combustion. The gas is generated in producers with step grates and led into the furnace through heating flues, at the upper end of which it is burnt by means of a current of air. The air is forced in by means of fans, and is heated in the brickwork of the furnace. The furnace may be worked either by draught produced by a stack, or by a blast underneath the grate, in which case air is also forced into the closed ashpit of the gas producers. The latter arrangement presents the advantage that the inferior small coal and dust may be used for the gas producers. The arrangement of such a furnace with heating flues is shown in Figs. 176 and 177. *G* are the two gas producers, provided with step grates *t*, into the ashpits of which air is blown through tubes *g*. The producer gas passes from the producers through flues *k* into the heating flues *h*. At the upper end of the latter the gas is mixed with the heated air required for combustion, which is forced in by means of fans or by injectors through the flue *z*, from which it passes through the flues *y*, *x* and *x'*, in which it is sufficiently warmed, and escapes through the pipes *d* and *d'*. The flame first rises to the roof and then descends, surrounding the muffles, and escapes through the apertures *f* into the flues *w*, whence the products of combustion pass into the stacks *e*, or into the main stack *H*. The blast for the producer is taken from the flue *z* by a branch flue *g*, opening into the ashpit of the producer; *m* are the muffles, *r* are the adapters, *u* are the openings through which the residues in the muffles are dropped into vaults provided with doors; *o* are the



calcining chambers built in between each pair of furnaces; *R, R* are annealing chambers. A double furnace with 64 muffles, as in use at the Hohenlohe Works, is shown in Figs. 178 and 179. Fig. 178 is a cross section through the furnace and producer; Fig. 179 a longitudinal section through the furnace. The furnace, which is

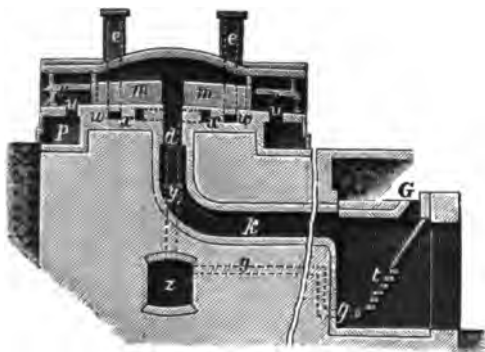


FIG. 178.

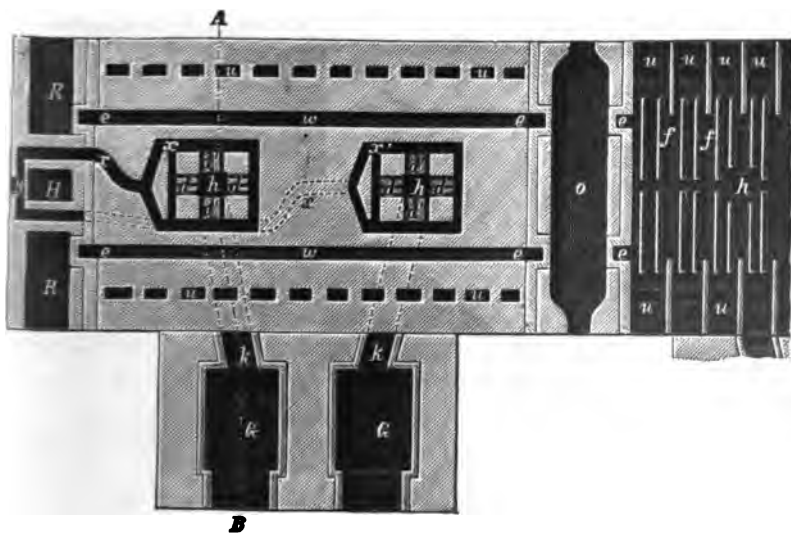


FIG. 179.

53 feet long and 18 feet 6 inches wide, is provided with 2 producers *S*, one to each 32 muffles. The producer gases pass through the flue *K* into 4 vertical shafts *G*, where they are burnt by the introduction of air. This air is forced by means of fans into the flue *Z*, passes from the latter into small flues *x* surrounding the heating flue, and from this through slots *F* into the heating shaft. The heating shaft

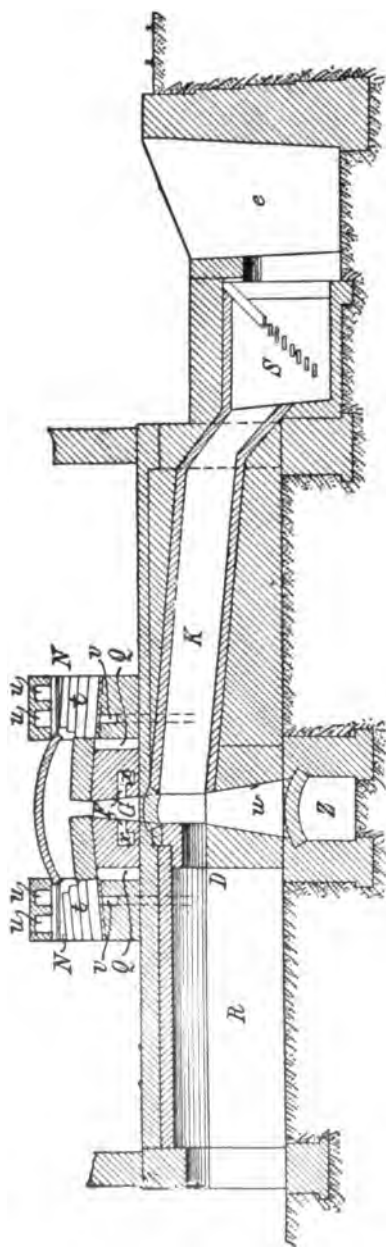


FIG. 178.

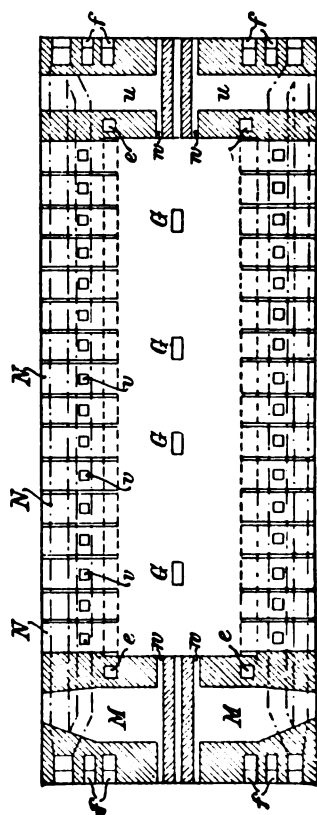


FIG. 179.

widens out below into the chamber *u*, so that any flue dust may be collected there. This chamber can be cleaned out through the vault

*R*, which is connected by a passage *D* with this chamber. After the flame has heated the muffles, it escapes chiefly through flues *w* at both ends of the furnace into the chambers *M* or *n* for annealing or calcining respectively, and from these chambers through the flues *f* into the stack. Such of the products of combustion as are not required for heating purposes pass directly out of the furnace through the apertures *e* into the stack. *N* are the recesses which contain the adapters of each pair of muffles, *Q* are flues in which any slag collects that may form when any of the muffles crack. By means of the shafts *v* the residues from the muffles are thrown into the vault *R*.

Lorenz<sup>1</sup> has proposed a modification of the Silesian gas furnace in which the gases and air do not enter through the floor of the furnace, but through its two end walls. The flames thus enter from either side of the furnace, pass between the muffles towards the centre, where they meet, surrounding the muffles and returning along the sides of the furnace to the end walls, whence they escape into flues. This furnace, which was in use at Lazy Works in Upper Silesia, has fallen out of use; for though it facilitates repairing of the heating shafts, yet it does not admit of uniform heating.

### *Gas Furnaces with Regenerators*

Furnaces on the Siemens principle are used in Upper Silesia. They require coal which shall not be in too small pieces. They admit of the uniform heating of large chambers to a very high degree of temperature, and in consequence thereof cause an economy of fuel and of muffles, and permit of longer campaigns than in the case of furnaces working without regenerators. On account, however, of their high first cost, of the necessity of employing better qualities of coals, of the care required in their management, of the readiness with which the flues in the regenerators become stopped up, of the difficulties connected with their heating, and of the high consumption of fireproof material caused by the regenerators, the application of the Siemens principle to distillation furnaces has been greatly limited, in spite of the above-named advantages. The general construction of a zinc distillation furnace on the Siemens

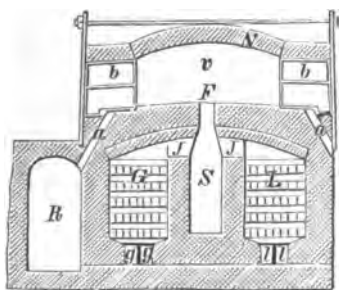


FIG. 180.

<sup>1</sup> *Steger, Preuss. Zeitschr. für Berg-, Hütten-, und Salinenwesen*, 1900, p. 403.

principle is shown in Figs. 180 and 181. *L* are the air regenerators, *G* the gas regenerators, *g, g* are the flues for the admission of gas and *l, l* for the admission of air to their respective regenerators. The gas and air, after being heated, pass through flues, *J J*, into the mixing

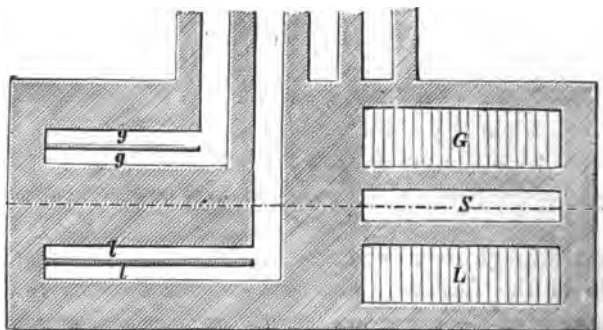


FIG. 181.

chamber *F*. The flame ascends first in one half of the heating chamber *v* up to the roof *N*, then enters the other half, where it descends, passing finally to the regenerators, which it traverses, and then escapes to the stack. The distillation residues from the muffles

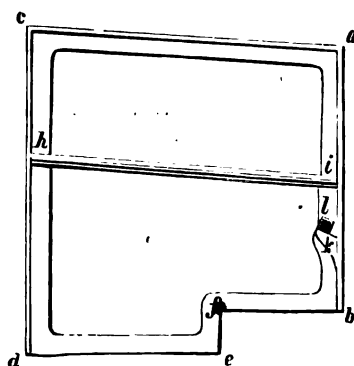


FIG. 182.

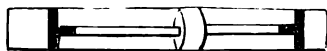


FIG. 183.

are dropped through the inclined shafts *a* into the vaults *R*. *S* is a pocket for the collection of flue dust; *b* are iron frames which replace the partition tiles of the recesses. They were designed by Cochlovius,<sup>1</sup> and are shown on a larger scale in Figs. 182 and 183 (each pair of recesses is otherwise separated by fireclay tiles 2 inches thick, known as partition tiles). The front side *a b* of the frame is secured to the buckstaves of the furnace, whilst the back portion *c d* rests against the furnace itself. The arch is carried by the upper portion *a c* of the frame. Of the lower portion of the frame, the portion *d e* is let into the furnace,

whilst *e f* lies against the floor of the furnace. A cross-bar *h i* serves to stiffen the frame. An iron rail lying upon a projection *k* replaces the step upon which the front portion of the adapter rests.

<sup>1</sup> D. R.-P. No. 9128.

The construction of the older zinc distillation furnaces at Freiberg is shown in Figs. 184 to 188. The regenerators lie under the furnace, and parallel to its longitudinal axis. *L* is one of the air regenerators, *G* one of the gas regenerators. The other pair of

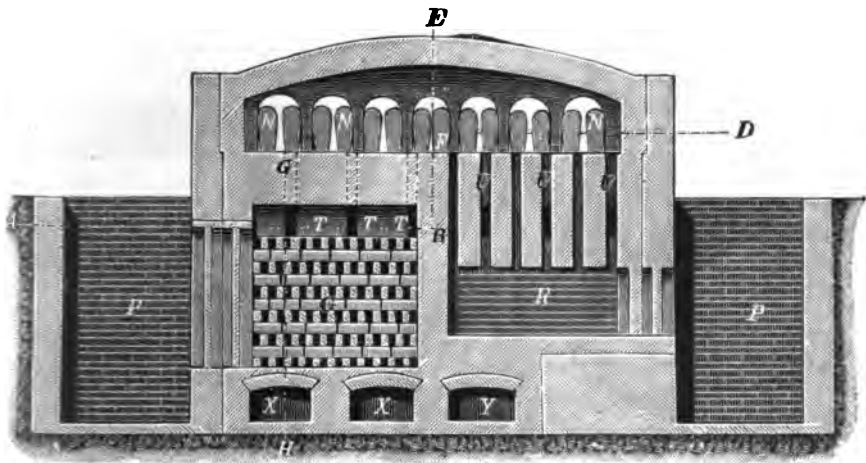


FIG. 184.

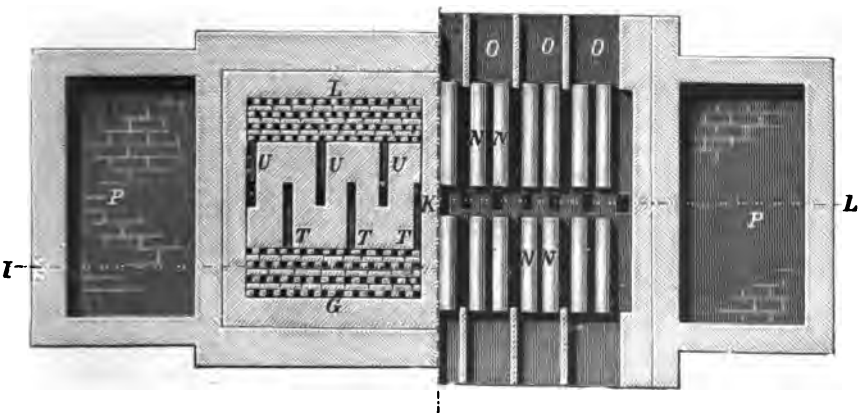


FIG. 185.

regenerators lying beneath the other half of the furnace is not visible in the figure. *W* is the reversing valve for the gas and *W*<sup>1</sup> for the air current. *X* are the gas flues, *Y* the air flues. The gas passes through *X* into the regenerator *G*, the air through *Y* into the regenerator *L*. At the upper portion of the regenerator the gas

escapes heated through three flues into corresponding vertical slots, whilst the air escapes at the upper end of the air regenerator through an equal number of flues *U* into its corresponding vertical slots. At the top of these slots the air and gas mix, the flame thus produced first surrounding two tiers of muffles on one side of the furnace, and then passing into the second half of the furnace, where it surrounds

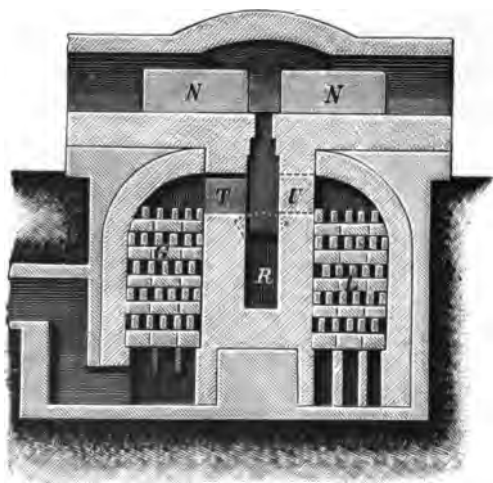


FIG. 186.

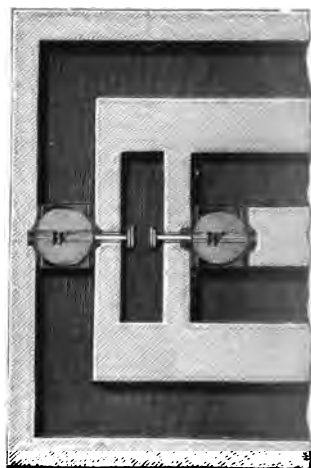


FIG. 187.

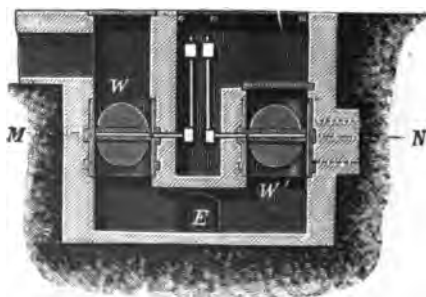


FIG. 188.

the muffles therein contained, and then escapes through the six air and gas slots in the floor of the furnace into the corresponding regenerators, from which it passes to the flue *E*, and thence to the stack. At definite intervals—from half an hour to an hour—the direction of the air and gas currents is reversed by means of the reversing valve, so that gas and air now ascend in the second half of the furnace, first heat the muffles contained therein, and then

take their way through the first half of the furnace to the first pair of regenerators, whence they escape to the stack. The air and gas slots are prolonged downwards into chambers or pockets *R*, into which any flue dust drops down and collects. By means of the chambers *P* the brickwork which forms the outer wall of the regenerators and pockets is accessible, so that these can be repaired and cleaned out when desired. *N* are the muffles, *O* are the recesses. The number of muffles in single furnaces of this kind amounts to 28 to 32, in double furnaces to 56 to 80. At the Bernhardt Works the number is 80. Furnaces on the Siemens principle have been used with good results at the Paul Wilhelmina Works, Bernhardt and Flora Works in Upper Silesia. The gas furnace with air regenerators of Haupt,<sup>1</sup> which are provided with regenerators along each side of the longitudinal axis of the furnace, in addition to calcining and tempering furnaces, and in which the hearth is heated both from above and below, do not seem to have come into use.

### *The Charge*

The charges for muffles are prepared in the same way as for retorts; calamine is not, however, submitted to distillation in the form of powder, but in pieces of the size of a hazel nut, so that the muffle charge, which is very much larger than that for the retort, shall not be too compact. In Upper Silesia the coal used for reduction is employed in the form of what is known as *cinder*, that is to say, after its gas has been got rid of. The cinder is obtained partly from puddling works, partly collected below the grates of the gas generators, and partly produced in special furnaces. For instance, at the Hohenlohe, Kunigunde, and Theresia Works, in Upper Silesia, coals of grain and pea size are heated in furnaces, whereby they partly coke and may agglomerate a little, according to their quality. At the Paul and Wilhelmina Works, near Schoppinitz, coals thus heated are also partially employed. In many works crushed coke is used. By driving the gas off from coals, from 63 to 72 per cent. of the weight of the latter is obtained as cinder. Of recent times the quantity of cinder in the charge in Upper Silesia has been continually on the increase; by these means the red-hot particles of coal in the charge are brought into intimate contact with the ores, and the formation of an atmosphere of carbon monoxide is at the same time promoted, so that any oxidising influence of carbon

<sup>1</sup> D. R.-P. No. 7425, *Oesterr. Zeitschr.* 1881, p. 336.

dioxide, water vapour, and air are prevented from affecting the zinc vapour. For example, at the Wilhelmina Works, the proportion of cinder amounts to almost 50 per cent. of the weight of the ore treated, or 34.9 per cent. of the total fuel used in the operation. The charge for one muffle is at present about 2 cwts. on the average for Upper Silesia.

### *Process of Distillation*

Before a furnace is put into operation, it is carefully dried and fired up slowly. In the case of the old Silesian furnaces, as soon as the furnace has attained the requisite temperature, the muffles which have been raised to a red heat in the annealing furnace are set in their places. The interspaces between the muffles and the columns are filled in with bricks and clay. The adapters are then attached to the muffles, and the openings in the lower portion of the muffle below the adapters are closed by the tiles previously mentioned. The charges are then gradually introduced through an opening in the bend of the adapter by means of a long scoop, which passes through the horizontal portion of the adapter into the muffle. The charge of the muffles, small at first, is gradually increased, until on the seventh day they are taking their full charge. The muffles that lie nearest the fire are more heavily charged than those farther away from it. After the muffle has been charged, the opening in the bend of the adapter is closed by means of a tile luted upon it; the sheet-iron doors in front of the recesses are closed; and the temperature of the furnace is raised to whiteness. Soon after the introduction of the charge, under ordinary circumstances, carbon dioxide, carbon monoxide, and water vapour are evolved, and zinc fume is deposited in the adapters as a result of the action of carbon dioxide and water vapour upon the zinc vapours, as also of the high degree of dilution of the latter by the above-named gases; in order to prevent the adapter from being clogged, it must be repeatedly cleaned out. Two to three hours after the charge has been introduced, carbon monoxide alone is contained in the escaping gases. As there are now no oxidising agents present, and as zinc vapour is contained in large quantities in the gas, condensation of zinc commences, attains its maximum after 6 to 8 hours, and remains stationary for another 6 to 8 hours. It then diminishes, and is concluded in a few hours longer. The total time of working off a charge, including charging, occupies 24 hours. When the distillation is complete, the front doors of the recesses are opened, and the tiles are removed from the charging openings. Any



fluid zinc that may still be remaining in the horizontal portion of the adapter is raked down into the condensing chamber, and the metal that is solidified in the latter is removed. The tile which closes the muffle below the step supporting the adapter is now removed by means of tongs and the residues of the distillation are drawn out by means of scrapers, any accretions upon the sides of the muffles being knocked off by means of an iron bar. Muffles that have become defective are changed, and others which may have been cracked, but which are still capable of being repaired, are luted with clay. The muffles are then charged afresh. The two rows of muffles are either charged one directly after the other or else the second row is charged some time, up to eight hours, after the first, in order to give the workmen time for a rest. By the latter method the uniform course of the process and the output of zinc are interfered with.

The process of distillation when new Silesian furnaces are employed agrees with the former, except as influenced by the different construction of these furnaces as regards the disposition of the muffles and the character of the adapters. The furnaces are heated up by means of a coal fire maintained upon the grates or in the gas producers. Furnaces on the Siemens principle are not heated up by means of the producer, but by means of a fire maintained upon a provisional grate inside the furnace itself. These grates are arranged in two recesses lying diagonally opposite to each other, whilst the other recesses are loosely bricked up during this period of heating up. After three or four days the muffles are put in their places, and annealed in the furnace itself. After the fire has been gradually increased for another three or four days, the grates are removed and gas is introduced from the producer, which has been carefully warmed up and fired, the requisite quantity of air for burning the gas being at the same time admitted. After gas-firing has thus been commenced, muffles previously heated to a red heat are introduced into the two recesses, which have now been set free for this purpose; the muffles are then bricked in, the adapters are attached, and the muffles charged. In the case of adapters of the bellied form, charging takes place through the front of the adapter, whilst with those having the shape of inclined cylindrical tubes or of rectangular boxes, the front of which is closed by a tile, or by a clayed iron plate, charging is performed through the apertures left when these plates are removed. If there are several tiers of muffles, the topmost tier of muffles is charged first. The first charges are very small and consist of readily reducible material, such as zinc fume and rich residues, the charges being gradually increased up to the normal,

which averages 2 cwts. for the big Silesian muffles. The time of working off a charge in this furnace amounts also to 24 hours. The temperature must be kept as uniform as possible during the process of distillation. Should it be too high, uncondensed zinc escapes through the adapters and burns in contact with the air; if it is too low, the zinc condenses as fume, which partly remains in the adapters and partly is carried off by the current of gas. In such a case the adapters in the old Silesian furnaces might possibly become stopped up by solid zinc. If any of the muffles crack, zinc vapour may either escape from the muffles into the furnace, or the furnace gases may enter the muffle, according to the ratio between the pressures inside the furnace and inside the muffle respectively. After the conclusion of distillation, zinc is removed from the adapters, the residues are then raked out, the muffles are repaired or replaced, and then charged once again. Zinc is raked out from the bellied adapters and collected in a ladle held beneath the latter. From the inclined cylindrical or rectangular adapters the metal is tapped out into iron ladles by removing the front plate. By means of these ladles, which are provided with spouts, the fluid zinc is cast into moulds. When several tiers of muffles have to be dealt with, the zinc is first collected from the uppermost tier of muffles. Herter<sup>1</sup> runs the zinc into transportable, externally heated vessels lined with fireproof material. These vessels can be tipped. Lead and zinc collect in them, forming two layers, which can be separated by means of a tap-hole in the bottom of the vessel.

## ECONOMIC RESULTS AND EXAMPLES OF ZINC EXTRACTION IN MUFFLES

### OLDER FURNACES FIRED DIRECT

#### *Old Silesian Muffle Furnaces*

In Upper Silesia, by means of old Silesian furnaces with 20 muffles in each, 15 cwts. of calamine were treated in 24 hours, and in furnaces with 24 and 26 muffles, 18 and 20 cwts. of calamine respectively. The output of zinc from the ore amounted to 14.07 per cent. For the production of 1 cwt. of zinc,  $7\frac{1}{4}$  cwts. of calamine and 35 cwts. of coals were required.

The muffles lasted 6 to 8 weeks.

<sup>1</sup> Brit. Pat. No. 8175, 1901.

*Silesian Furnaces Fired by Grates*

At the Silesia Works, near Lipine,<sup>1</sup> the older furnaces, working with flat grates and blast in the ashpit, contained each 24 muffles, 21·6 inches high and 7·2 inches broad. The charge of a furnace amounted to 4,116 lb., yielding an output of 917 lb. of zinc per 24 hours. For each cwt. of zinc, 48 cubic feet of coals and 0·10 muffle were consumed.

*Furnaces Fired with Gas*

Modern furnaces in Upper Silesia fired by gas consume at present some 10 cwts. of coal, of which 7 cwts. is used as fuel, for each cwt. of zinc produced, the charge containing 20 per cent. of zinc, and the average weight of charge to each muffle being 227 lb. The weight of coal used for reduction amounts to about 40 per cent. of the weight of the ore, or about 2·8 cwts. per cwt. of zinc. Of this coal, 1 cwt. consists of cinders or of coke from the gas producers. In 1870, the consumption of coal amounted to 19·16 cwts., and in 1880 to 12·41 cwts. per cwt. of zinc. Rather less than 4 cwts. of clay are consumed to each ton of zinc. For each 13 or 14 muffles 1 workman is required per 24 hours, or 4 to 5 men for the production of 1 ton of zinc in this time. The loss of zinc amounts to 25 to 30 per cent. The residues of distillation contain 3 to 3·5 per cent. of zinc. Of the above loss, 12 to 15 per cent. is due to the zinc retained in the residues and 10 to 15 per cent. to volatilisation. Each muffle yields 10 to 12 cwts. of crude zinc.

At the Hohenlohe Works, in Upper Silesia, where single-storied furnaces with 32 muffles are used, each 22 inches high, 6 inches wide, 4 feet 9 inches long over the gas shafts, the others being 5 feet 5 inches long, the charge consists of 17 cwts. of calcined blende, containing 42 to 45 per cent. of zinc, 5 cwts. of calamine in small pieces, containing 26 to 32 per cent. of zinc and 21 cwts. of calamine slimes, containing 14 to 16 per cent. of zinc, or altogether 2·3 tons of ore; the yield in 24 hours amounts to 1,080 lb. of zinc. During this period 3 tons 7 cwts. of coal were consumed in the process, or 6·83 lb. of fuel to the lb. of crude zinc.

At the Silesia Works, near Lipine,<sup>2</sup> there are at present furnaces in use, which are built with two gas shafts, to carry 32 to 40 muffles, 16 or 20 respectively on either side. There is a separate producer to each furnace. The air employed for combustion is blown in by means of

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1867, p. 340.

<sup>2</sup> Kindly communicated by the factory inspector, Scherbening, of Lipine.

a fan and mixed with gas, 1 foot 8 inches below the upper edge of the shafts. The dimensions of the muffles and their thicknesses are shown in Figs. 189 and 190. The fragments of muffles are obtained by grinding old muffles down to a mesh of 0.23 to 0.27 inch. The

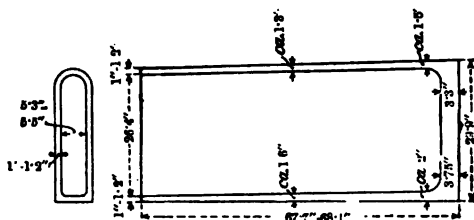


FIG. 190.

FIG. 189.

charge consists of 25 to 45 parts of calamine and 75 to 55 parts of calcined blende, according to the quantities of these respective ores that may happen to be available. The reducing agent consists of cinders, the quantity of which amounts to 45 to 47 per cent. of the weight of the ores. The charge for a muffle amounts to 198 lb. The period occupied in distillation is 16 to 17 hours, that for the remaining operations 7 to 8 hours. A muffle will last between 35 and 47 days, depending chiefly upon the age of the furnace, and therefore upon the greater or lesser solidity of the muffle seat, and upon the ratio of zinc blende contained in the charge, zinc blende requiring a higher temperature than calamine. The output of a furnace in 24 hours amounts to 6,350 lb. of ore for 32 muffles and 7,940 lb. for 40. The consumption of fuel per ton of ore varies from 1 to 1.2 tons; per ton of zinc it amounts to 5.5 tons. The fuel used is partly duff, partly very slaty coarse coal; the consumption of reducing agent amounts to 2 tons per ton of zinc, and 2 muffles are destroyed per ton of zinc. The output of zinc is 77 to 80 per cent. of that present in the ore, or 20 per cent. of the weight of the latter. The loss of zinc varies from 20 to 23 per cent.

At the Paul Works, near Rosdzin, there are at present in use Siemens furnaces and gas-fired furnaces using blast in the ashpit. Each furnace has its own producer and one or two heating shafts. The number of muffles amounts to 32. Air is introduced below the grate of the producer by means of a fan in order to generate gas, as also under the body of the furnace to burn the gases. The muffles are made of a mixture of 65 per cent. of clay and 35 per cent. of muffle fragments. The ore mixture contains 30 per cent. of calcined blende and 70 per cent. of calcined calamine; the reducing agent—cinder—amounts to 40 per cent. of the weight of the ore. Each muffle takes a charge of 2 cwts. The time required for treating a charge, including recharging the muffles, is 24 hours. The muffles

will stand from 40 to 50 days. A furnace with 32 muffles will treat on the average 3 tons of ore in 24 hours, extracting 8 to 10 cwts. of zinc. The consumption of fuel in this time amounts to about 4 tons = 1.33 tons of coal per ton of ore, or 8 to 10 parts of coal to 1 part of zinc. The output of zinc is about 13 per cent. of the weight of the ore, the loss of zinc amounting to 21 per cent.

### *Furnaces with Regenerators*

The distillation furnace at Freiberg, on the Siemens principle, has 32 muffles disposed in two rows of 16 each; they are 5 feet 2 inches long, 9½ inches wide, and 19½ inches high. The charge for a muffle consists of 1 cwt. of calcined blende, containing 33 per cent. of zinc, and 25 per cent. of lignite coke. The process of distillation lasts 24 hours, the consumption per cwt. of blende amounting to 5.3 cubic feet of fuel. The weekly output of the furnace is 2½ tons of zinc and 5 cwts. of zinc fume, containing 90 per cent. of zinc. The output of zinc amounts to 70 per cent. The distillation residues contain 10 per cent. of zinc; they carry silver, and are smelted with lead for the extraction of the silver.

At the Paul Works, near Rosdzin, Siemens furnaces are used carrying 60 to 72 muffles, 5 feet 7 inches to 5 feet 11 inches long. Two producers are attached to each furnace. The muffles are made of a mixture of 65 per cent. of clay and 35 per cent. of fragments of old muffles. The ore charge consists of 30 per cent. of blende and 70 per cent. of calamine, the reducing agent—cinder—amounting to 40 per cent. of the weight of the ore. The charge for a muffle consists of 220 to 242 lb. The total period of distillation, including the necessary operations, amounts to 24 hours. A muffle lasts 40 to 50 days on the average. A furnace with 60 muffles treats 6 tons of ore in 24 hours, extracting about 1 ton of zinc. The consumption of fuel during this period amounts to 6.1 tons = 1.016 tons per ton of ore, or 6.1 tons per ton of zinc. The consumption of cinder for reduction amounts to 8 cwts. per ton of ore, or 2.4 tons to the ton of zinc. The consumption of muffles amounts to 1.35 per ton of zinc. The output of zinc is 13 per cent. of the weight of the ores. The Siemens furnaces require a better quality of fuel than is needed for ordinary furnaces using blast in the ashpit; the former, however, work more uniformly and consume less fuel than do the latter. The advantage of the Siemens furnace are shown from the following table

of the working results of the grate-fired furnace and the Siemens furnace at the Paul Works for the year 1895:—

	Grate furnace with 82 muffles. Tons.	Siemens furnace with 60 muffles. Tons.
Ore treated per furnace per 24 hours . . .	3	6
Consumption of fuel per ton of ore . . . .	1.33	1.016
Consumption of muffles per 5 tons of ore .	1.6	1
Percentage of zinc extracted from the ore .	13	13

### III.—DISTILLATION IN BELGO-SILESIA FURNACES

In these furnaces the muffles lie in two or three horizontal tiers. Firing is by gas, except in Belgium, where long-flaming coal is available.

In the newer works the muffles have the form shown in Fig. 191. Their length in the clear is from 4 feet to 4 feet 7 inches, the

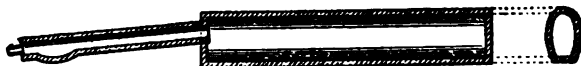


FIG. 191.

width 6 to 6½ inches, the height 10 to 12 inches, and the thickness of wall 1 inch on the average. They are prepared by machinery. The older hand-made muffles are 5 feet 6 inches long, 9 inches wide, and 1 foot 5 inches high.

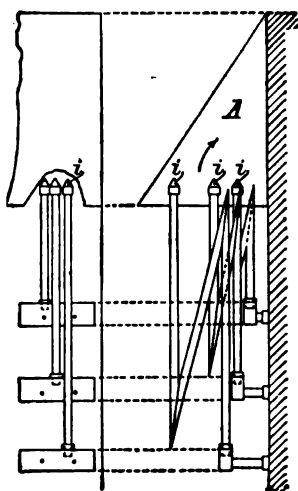


FIG. 192.

The material from which these are made has been fully described above. To give examples: at the Hamborn Works it consists of 60 parts of burnt and 35 parts of unburnt Belgian clay and 5 parts of coke; at the Birkengang Works, near Stolberg, it consists of  $\frac{2}{3}$  burnt and  $\frac{1}{3}$  unburnt Belgian clay; and at Dortmund of 2 parts of burnt clay, 1 part of unburnt clay, and  $\frac{1}{10}$  part of powdered coke. The crushing, mixing, and preparation of these muffles, and the hydraulic machines used, are the same as described above under the Belgian furnaces, and the drying of the retorts is carried out as explained under the Silesian furnaces. The adapters are usually bellied out below, as shown in Figs. 146 and 191. They are made as described on page 139. The nozzles are flat-lying ones, like those used in the Belgian and Silesian furnaces. Vertical nozzle

cannot be employed, since the lower ones would interfere with the fixing of those above. Combined horizontal and upright nozzles, like those of Steger, may be employed. Fig. 192 shows the method of fixing these. The gases evolved pass through the openings *i*, where they burn, and then pass on through the flue *A* to the outside.

### *The Distillation Furnaces*

Furnaces with grate-firing are still used in Belgium, but in Germany gas-firing alone is employed. An old grate-fired furnace is shown in Fig. 193, where *x* are the upper and *y* the lower muffles, and *z* the adapters. The flame passes up from the grate *r*, and envelopes the muffles, and escapes through flues *k* to the stack. The

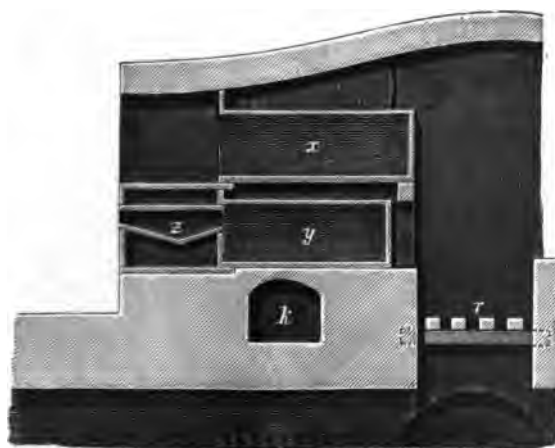


FIG. 193.

upper muffles are 4 inches longer than the lower, their dimensions being 6 feet in length, 10 inches in width, and 1 foot 8 inches in height. Between the recesses, which are 3 feet deep, are supports of firebrick. Siemens firing is but exceptionally used in gas-fired furnaces. In most of these furnaces the air is first warmed, either in flues in the gas generator or, as is more usual at present, in regenerators. Each furnace holds up to 252 muffles.

The construction of a gas furnace with muffles arranged in two tiers is shown in Figs. 194 and 195. The gas is produced in a Böttius generator, and the air is heated in the flues *l*, the two being mixed at *o*, where the gas issues from the generator. The flame first rises to the roof, and then descends through the flues *a*, which are built between each pair of recesses, into the flue *b*, which conducts

the products of combustion into the stack; *m m* are the muffles placed in two tiers one above the other.

The distillation residues are dropped into the shaft *R*; when these residues are being drawn out from the lower muffles, the tiles that close the upper portion of the vertical flues are removed, and when

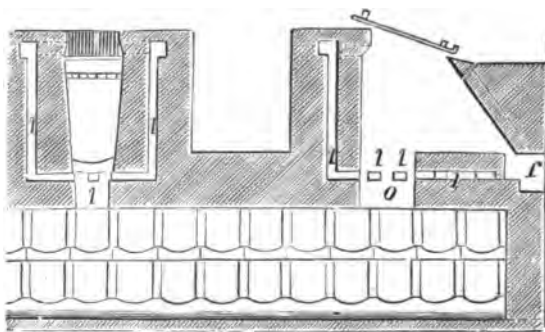


FIG. 194.

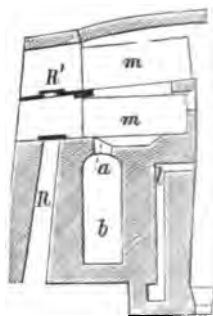


FIG. 195.

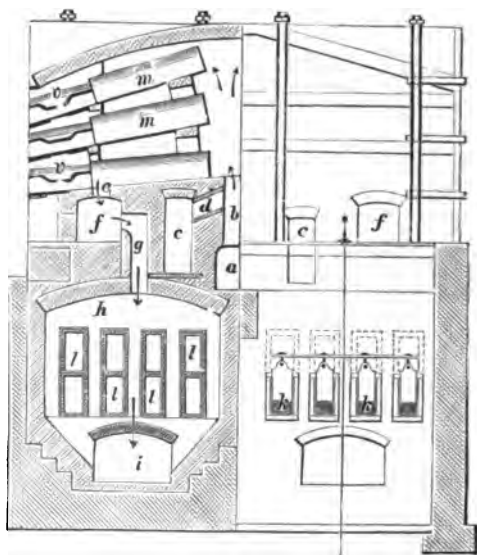


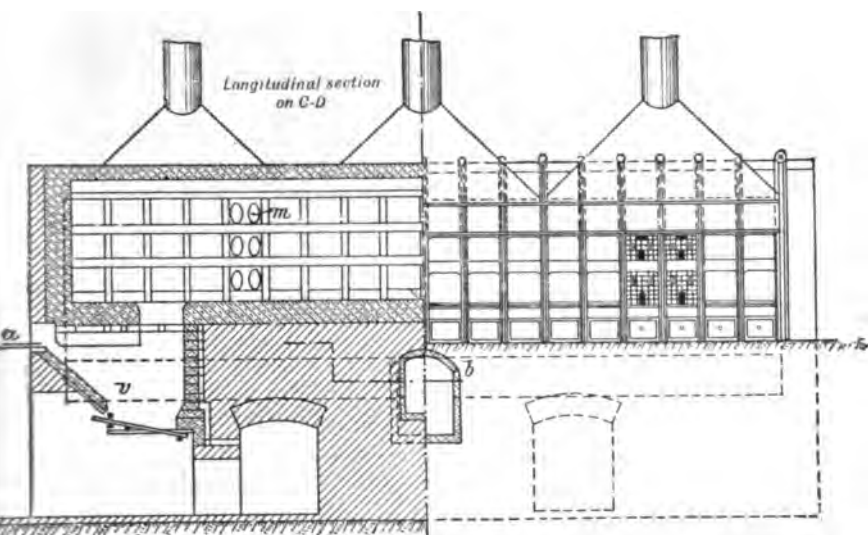
FIG. 196.

the residues have to be removed from the upper muffles, the tiles *R* are removed also. The Boëtius producer has given satisfactory results, and is being successfully used at the works in the Rhine Provinces.

Fig. 196 shows the construction of a furnace with three tiers of muffles; *m* are the muffles, *v* are the adapters; the lowermost muffles



lie for their full lengths upon the hearth and project for some 2 inches into the recesses. The muffles of the two upper tiers are also supported in front in the recesses, their back ends lying upon supports made of exceedingly fireproof material. The gas which is developed in the producer, not shown in the figure, enters through the flue *a* into the vertical shaft *b*, at the upper end of which it is burnt by means of hot air there introduced from the outside through the flues *l*. The quantity of air can be regulated by means of dampers *k*, at the mouth of the latter. Through the flues *l* the air passes into the flue *c*, and from the latter through *d* into *b*. The flame rises first to the roof, and then returns, escaping through apertures *e* into



FIGS. 197 and 198.

the flue *f*, thence through the vertical flue *g* into the large horizontal flue *h*, and from the latter into the flue *i* leading to the stack. In its passage through the flue *h* the products of combustion surround the air flues *l* and thus heat the air to be used for combustion.

The construction of a furnace of the most recent type with oval muffles, such as are at present in use in the Rhine Provinces, is shown in Figs. 197 to 201,<sup>1</sup> Fig. 197 being a longitudinal section on *c d*, Fig. 198 a front elevation, Fig. 199 a cross section on *e f*, Fig. 200 a sectional plan on *a b*, and Fig. 201 on *g h*; *m* are the muffles, *v* the adapters. There are 108 muffles in each side of the furnace block, or 218 in all. There is a gas producer *v* at each of the short

<sup>1</sup> Dürre, *Ziele und Grenzen der Elektro-metallurgie*, p. 207, Leipzig, 1896.

sides of the furnace; the air for the combustion of the producer gas undergoes previous heating in the walls of the producer as indicated in the figures. The products of combustion, after heating the muffles, escape through the vertical flues *w* into the main flues *z*, which communicate with the stacks.

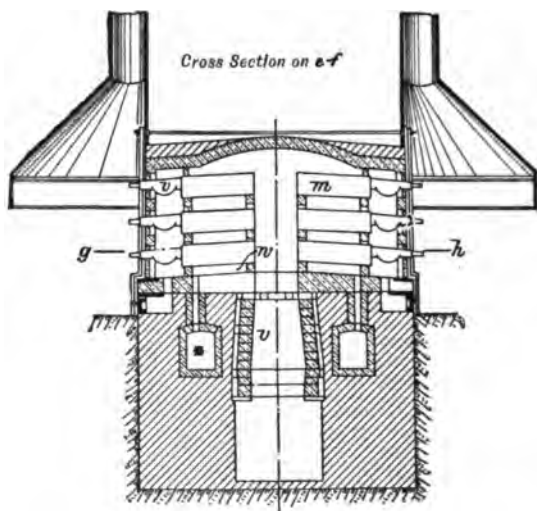
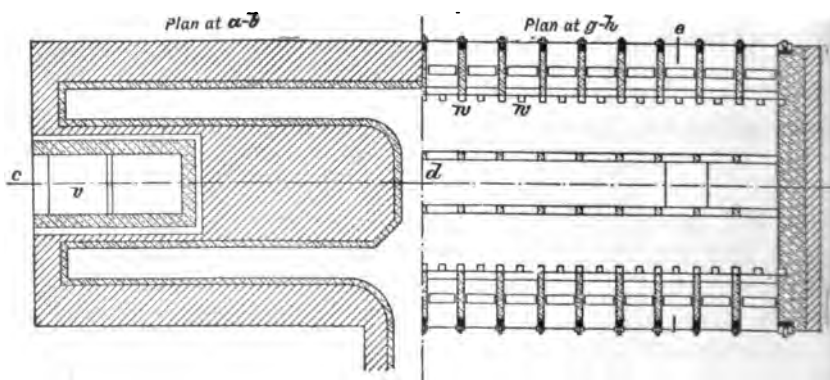


FIG. 199.



FIGS. 200 and 201.

Nolte and Beringhofen<sup>1</sup> propose to effect the uniform heating of direct-fired Belgo-Silesian furnaces by closing the otherwise open generator chamber with an arch, and by allowing the hot gases, after mixing with air, to pass through a series of holes on each side of the

<sup>1</sup> *Zeitschr. für das Berg-, Hüttenm., und Salinenwesen*, vol. xlviii. p. 404.

arch. Two lines of flame would be thus formed, and the retorts would get uniformly heated.

The charge for the Belgo-Silesian furnaces is prepared in the same manner as for the Belgian and Silesian furnaces.

Binon and Grandfils<sup>1</sup> have also proposed the employment of charges mixed with tar and moulded into blocks for muffles. According to their views, by the employment of blocks moulded to the shape of the muffle, 50 per cent. more charge can be introduced into it than by the ordinary method of charging.

Schulte<sup>2</sup> mixes the ore before addition of the coal with 3 per cent. of tar. Picard and Sulman<sup>3</sup> also use tar. Each muffle receives a charge of from 60 to 77 lb., the upper tiers being charged first. The process of distillation resembles the Silesian process, with slight differences due to variation in the construction of the furnaces and adapters. Each charge takes about 24 hours to work off. The consumption of coal (for reduction and heating) and clay, in the case of the modern furnaces in the Rhine Provinces and Westphalia, is 3 to 4 tons and 440 lb. respectively per ton of zinc, for ores containing 50 per cent. of zinc, and for muffle charges of 75 lb. One workman is required for 13 to 14 retorts.

#### *Examples of Zinc Extraction in Belgo-Silesian Furnaces*

At the works of the Berzelius Company, near Gladbach, there are three tiers of small muffles; the furnaces are gas-fired and the air is heated in regenerators. A furnace block holds 208 muffles, which are emptied every 24 hours, there being 12 men engaged during that time. The charge consists of calcined blende, containing 52 per cent. of zinc, and of cinder. Each muffle receives a charge of 55 lb. of ore and 18 lb. of cinder. The charge for the furnace amounts to 52 tons of ore and 1.664 tons of cinder, the output per 24 hours amounting to 2.4 tons of zinc, with a loss of 10 to 13 per cent. Muffles will last from 45 to 60 charges. For each cwt. of zinc 3.9 tons of coal for fuel and for reduction are consumed.

At the Neumühl-Hamborn Works, near Oberhausen, furnaces are employed with producers in which the air is heated. These furnaces are double furnaces containing on each side three tiers of muffles, each now containing 42 muffles and each side of the furnace 126, so that the entire furnace takes 252 muffles. Each such furnace has two producers, one at either end. The muffles are upon the average 4 feet

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1883, p. 198-211; 1882, p. 531; 1881, p. 27.

<sup>2</sup> U.S. Pat. 718222, January 13, 1903.      <sup>3</sup> U.S. Pat. 665774, January 8, 1901.

7 inches long,  $6\frac{1}{2}$  inches broad, and 12 inches high in the clear, and are made of a mixture of about 30 parts of calcined Belgian clay, 35 parts of raw Belgian clay, and 5 parts of coke. The charge consists chiefly of calcined blende, containing 53 to 55 per cent. of zinc. The coal used as a reducing agent, amounting to 40 to 42 per cent. of the weight of the calcined ore, consists of coarse siftings from the lean coal of the basin of the Ruhr. The charge for a muffle consists of 66 to 73 lb. of ore and 29 lb. of coal, as also of a small quantity of skimmings and residues. The total charge for a double furnace consists of 7·6 to 8 tons of ore, exclusive of the skimmings and residues of the previous day. The distillation lasts 19 hours, 5 hours being employed in cleaning up and charging. The consumption of fuel amounts to 12 tons per furnace per 24 hours; this fuel is a coal slack giving a long flame and containing 22 per cent. of ash. With a good quality of coal, such as is being used in other works in the Rhine Provinces and Westphalia, one-third less coal would be required. For each ton of zinc 3·6 tons of coal are used for fuel and 0·88 for reduction. A muffle lasts 30 days on the average, 8 muffles being destroyed per day per furnace. During 6 hours in which the muffles are being emptied and recharged 12 men are engaged; during the period of reduction 2 men, who work a 12-hour shift.

At the Münsterbusch Works, near Stolberg, furnaces are also at work provided with air regenerators. To each furnace block there are two producers, one at either short end. There are three tiers of muffles of 80 each, or 240 altogether. The latter are 4 feet to 4 feet 7 inches long, and take a charge of 75 lb. of calcined ore and 31 lb. of coal. They are made of a mixture of 60 per cent. of burnt and 40 per cent. of raw Belgian clay, to which coke dust is added. The zinc contents of the charge amount to 52 to 54 per cent., a lean coal being used as the reducing agent, and its weight being 40 per cent. of that of the calcined ore. The time required for distillation, including that of charging, is 24 hours. Each block will treat some 8 tons of calcined ore in this time, with a consumption of 8·5 to 9·2 tons of coal as fuel. For 1 ton of zinc about 2·5 tons of coal are used for fuel and 1 ton for reduction. A muffle will last, according to the quantity of iron and coke contained in the charge, from 40 to 50 days. A furnace block with 240 muffles requires 14 furnacemen, working for 8 hours, 2 firemen working for 12 hours, 2 lads working for 12 hours, and 1 labourer for wheeling ore, coal, and residues.

At the Birkengang Works, near Stolberg, furnaces on the Siemens principle were in use containing three tiers of muffles. They were built together in pairs, their longer sides adjoining. Each row consisted

of 18 muffles, so that the double furnace contained 54 muffles on either side, or 108 altogether. The charge consisted of blende, and contained 52 to 53 per cent. of zinc. The total ore charge of a double furnace amounted to 4.9 tons. The distillation lasted 24 hours, 1.2 tons of fuel being consumed to each ton of ore. The men employed per furnace per 24 hours numbered 10, who worked 10 hour shifts. A muffle lasted on the average 40 days.

*Losses of Zinc in Treating Zinc Ores in Retorts and Muffles*

As has been repeatedly stated, the losses of zinc in the process of distillation are very high compared to the losses in the extraction of other metals. They amount to 10 to 25 per cent. of the zinc contents of the ore, and only in very exceptional cases fall below 10 per cent. In the Rhine Provinces, Westphalia and Belgium, where ores averaging 45 per cent. of zinc are treated in retorts and small muffles, the losses average some 12 per cent. of the zinc contents of the ore. In Upper Silesia, where ores containing 20 per cent. of zinc are worked in large muffles, they amount to 25 per cent. of the zinc contents of the ore. In Freiberg, where blende containing 30 to 31 per cent. of zinc is worked in small Silesian muffles, they amount to 18 per cent. The loss of zinc at the works of the Vieille Montagne at Angleur, in Belgium, amounts to 10 per cent.; at the Bleyberg works, in Belgium, to 13 to 14 per cent.; at Münsterbusch, near Stolberg, to 10 per cent.; at Bergisch-Gladbach to 10 to 13 per cent.; at the Wilhelmina Works in Upper Silesia to 21 per cent.; and at many other works in that district to 25 per cent. These losses are due to the passage of zinc into the material of which the retorts consist, the escape of zinc through the pores of the retorts, and through cracks in the retorts, or from the retort breaking completely, through the escape of uncondensed zinc out of the adapters, through zinc remaining behind in the retort residues, and through the escape of zinc vapours when the residues are being removed from the retorts. The source of greatest loss is the retention of zinc by the distillation residues; next to that comes loss by volatilisation. Retorts newly introduced into the furnace only give their normal output of zinc after the lapse of several days, because their walls absorb a certain quantity of zinc at first. This metal combines with the clay of the retort to form an aluminate—an artificial zinc spinel. This compound gives the material of the retorts the well-known blue colour. The average zinc contents of old retorts, no longer fit for use, amounts to 6 per cent. It may, however, as has been shown at the

Bethlehem Works in Pennsylvania, rise to 21 per cent. According to Jensch,<sup>1</sup> seven samples of broken retorts from Upper Silesian works contained the following quantities of zinc oxide (per cent.):—17·64, 16·38, 14·11, 18·21, 16·63, 13·18, 15·96. The mean of these is 16·02, and this corresponds to 12·87 per cent. of zinc. By the addition of coke to the material of which the retorts are made, and by their manufacture under heavy pressure, the absorption of zinc has been greatly reduced at the works on the Rhine and in Belgium. Retorts, especially when not made under heavy pressure, are porous, and allow zinc vapour to escape through their pores owing to the pressure in the retort during the process of distillation. These vapours escape into the furnace and pass away with the products of combustion. If the pressure in the retorts is low, and that of the burning gases inside the furnace high, these gases and air penetrate into the retorts through the walls of the latter, and exert an oxidising action upon the zinc vapours in consequence of the oxygen and carbon dioxide which they contain. In order to avoid these defects, the retorts have been glazed, but this method has been shown to be less effective than that of manufacturing retorts under hydraulic pressure. In fact, this method of manufacturing retorts must be looked upon as an important improvement in the direction of diminishing the losses of zinc due to the porosity of the retorts. Great losses of zinc are caused by the cracking or breaking of the retorts, as in these cases zinc vapours escape freely from the retorts into the furnace, and where regenerators are used, may cause the passages in the latter to be stopped up. The loss of zinc due to this cause is greater the lower the durability of the retorts. Upon the average, retorts, as also both small and large muffles, last some 40 days. Out of 100 retorts in use, 2 are broken per diem at Angleur in Belgium; 3 in Ampsin in Belgium; 2 (small muffles) at Münsterbusch; 2·5 (large muffles) at Hohenlohe; 2·6 (large muffles) at the Silesia Works in Lipine. The fact that retorts and small muffles manufactured under pressure in Belgium and the Rhine districts are not more durable than the large ones made by hand in Silesia is due to the circumstance that retorts and small muffles are only supported at their two ends and have to resist a very intense heat. Nevertheless the durability of retorts and small muffles is increased markedly in consequence of this method of manufacture, seeing that their average life used formerly only to be 25 days. The loss of zinc due to the escape of its vapour from the adapter has been diminished to some extent by improvements in the

<sup>1</sup> *Op. cit.* p. 216.

latter, such as those of Kleeman, Dagner and Steger, but is still very considerable. The loss due to the escape of zinc vapour from the retorts whilst the residues are being removed from the latter has not been avoided up to the present. It is generally assumed that the loss due to volatilisation of zinc owing to the above causes, amounts to half of the total loss. The loss of zinc due to the remaining of metal in the distillation residues in the retorts is also very high, seeing that these contain 2 to 8 per cent. of zinc. This loss is greater, the less the zinc contents of the ore. In Upper Silesia, where the average proportion of zinc in the ore treated amounts to 20 per cent., the retort residues are not allowed to retain more than 3 to 4 per cent. of zinc; whilst in Belgium and the Rhine Provinces, where the ores average 45 per cent. of zinc, it may average 4 to 5 per cent. The zinc which enters the retorts in the form of sulphide is not reduced, and, therefore, increases the zinc contents of the residues. Dead roasting of zinc blende is, therefore, an indispensable condition for good working. According to Firket the distillation residues from the Belgian furnaces for the year 1898, contained on an average 4.1 per cent. of zinc, 5.5 of lead and 0.0209 of silver, and their weight amounted to 65 to 70 per cent. of the ore and other zinciferous materials treated. In a Belgian works 680 cwts. of residues were obtained from 1,000 cwts. of charge, made up of 460 cwts. of roasted blende, 410 cwts. of calcined calamine, and 130 cwts. of zinc-bearing refuse. This was mixed with 400 cwts. of coal, for reduction purposes, containing 9 per cent. of ash, 8.5 of volatile matter, and 82.5 per cent. of fixed carbon. The composition per cent. of the charge was:—zinc 40 to 50, lead 6 to 7, silver 0.004 to 0.005, iron 15 to 18, sulphur 1 to 1.5, and the residues contained: zinc sulphide 4, zinc sulphate 0.09, metallic lead 3.1, silver 0.006, lead oxide 1.91, metallic iron 5.69, sulphide of iron 2.48, ferrous and ferric oxide 15.57, carbon 18.07, besides silica, alumina, lime, magnesia, and traces of lead sulphate. The oxides of iron, lead, lime, magnesia and alumina were combined with silica. It is especially noteworthy that there was no zinc oxide present in the residues.

In America,<sup>1</sup> the ores used contain 60 to 70 per cent. of zinc, and the residue at but few works contains under 7 per cent. of zinc. Before the introduction of gas-firing the percentage was 10 to 12. The slags formed in the retorts from the coal ash and the gangue of the ore, only contain a little zinc as oxide; probably a portion is present as sulphide. The following analysis of a retort slag is given by

<sup>1</sup> Ingalls, *op. cit.* p. 538.

Rissman,<sup>1</sup> from a works near Pittsburg, at which mixtures of zinc blende and Smithsonite ores are smelted.

	Per cent.		Per cent.
Silica . . . . .	69·72	Magnesia . . . . .	1·84
Alumina . . . . .	10·08	Sodium oxide . . . .	3·44
Ferrous oxide . . . .	9·03	Zinc . . . . .	2·40
Lime . . . . .	6·17	Sulphur . . . . .	0·91

Rissman assumes that all the sulphur is combined with zinc, so that there remains only 0·68 per cent. of zinc oxide. The sodium in the slags arises from the retort glaze. Further analysis of slags by Rissman give 3 to 7·42 per cent of zinc. Thus it appears that slags containing much silica are only able to take up small quantities of zinc oxide. In spite of the very high losses of zinc which still obtain, the advances that have been made towards their diminution deserve recognition: and it must not be forgotten that whilst in the Rhine Provinces, Belgium and Westphalia, where retorts and small muffles are used, treating ores with 45 per cent of zinc, the loss of zinc with good working formerly amounted to 18 to 22 per cent., at present it does not exceed 10 to 13 per cent. On account of the poorer ore treated in Upper Silesia, the losses in that Province are naturally far higher than on the Rhine or in Belgium. If the zinc contents in the distillation residues be assumed to average 4 per cent., as is the case on the Rhine and in Silesia, the ores of the Rhine containing 40 per cent. of zinc would thus lose 10 per cent., whilst in Upper Silesia, where the charge contains a minimum of 18 per cent., the loss would amount to 23 per cent.

#### *Data for Calculating the Cost of the Distillation of Zinc*

The costs of zinc distillation comprise the costs of fuel, clay, wages and repairs. Under the Belgian method, ores containing 50 per cent. of zinc are treated, and with a charge of 63 lbs. per retort 3 to 4 tons of coal are at present consumed per ton of zinc, whereas the consumption formerly amounted to 7 to 8 tons. The consumption of fire-clay amounts to 4 cwts. per ton of zinc, including the clay required for retorts, adapters, fire-bricks and furnace repairs. One man is required per 24 hours to each 14 retorts, or 5·8 men to the ton of zinc. In the Belgo-Silesian process, with several tiers of small muffles one above the other, taking charges of 75 lbs. per muffle, in Belgium, the Rhine Provinces and Westphalia, ores with 40 to 50 per cent. of zinc consume the same amounts of coal and

<sup>1</sup> Ingalls, *Ibid.*



fire-clay per ton of zinc as in the Belgian furnace. One man is required per 24 hours for 13·3 muffles, or 4·8 men to the ton of zinc. In the Silesian process, with large muffles lying in one row, and taking charges of 227 lbs. each, the ores averaging 20 per cent. of zinc, the actual consumption of coal used per ton of zinc, including that required for reduction, amounts to 10 tons, of which 7 are consumed in heating. The coal used for reduction amounts to 40 per cent. of the weight of ore, that is, 2·8 tons are used to 1 ton of zinc. Of this, part is cinder and coke from the gas generators. In 1870 the coal consumption per ton of zinc was 19·16 tons, and even in 1880 it amounted to 12·41 tons. The consumption of clay is somewhat less than in Belgium and on the Rhine, being about 4 cwts. per ton. In 24 hours 1 man is required for every 13·6 muffles, or 4·5 men for 1 ton of zinc. With regard to the labour required about the furnaces of the various systems, it must be remembered that after the furnace has been emptied, cleaned and re-charged, which takes place once in 24 hours, it also requires firing, and wheeling in ore and coal, as also wheeling out the various products and residues. Emptying, cleaning, and re-charging the muffles of a furnace takes, for example, 6 to 8 hours for a Belgo-Silesian furnace, so that the working time of the actual furnacemen does not much exceed this period. A Belgo-Silesian furnace block, containing 200 to 240 retorts, would require, for example, per 24 hours, 12 to 14 furnacemen working 6 to 8 hours each; 2 firemen, 1 per 12 hours; 2 helpers (16 to 17 years old), 1 per 12 hours; and 1 labourer for wheeling in and wheeling out various materials, working 12 hours. This makes 17 to 19 workmen for 240 retorts per 24 hours, or 1 man for 12·6 to 14 retorts. The conditions in Belgium and Upper Silesia<sup>1</sup> are somewhat similar.

### EXTRACTION OF ZINC FROM FURNACE PRODUCTS

The furnace products rich in zinc which form the object of zinc extraction are the following:—Zinc fume (*poussière*); zinciferous flue dust; residues from the adapters and distillation apparatus; so-called furnace calamine, or furnace accretions and deposits containing zinc, which are formed when lead, copper, silver and iron ores containing zinc are smelted; zinciferous skimmings, and calcined zinciferous silver ores. Among the bye-products may be named zinc-silver alloys, zinc-

<sup>1</sup> Ingalls, *op. cit.*, p. 595.

lead-silver alloys, and zinc-copper-lead-silver alloys. As a rule these substances, with the exception of the various alloys of zinc with lead and the noble metals, from which the zinc is obtained as a by-product, are added to the charge during the zinc distillation, if necessary after undergoing suitable preparation. The above substances are but rarely treated by themselves in the retorts of zinc distillation furnaces, as a less pure zinc would thus be produced. Zinc fume is treated in some works in special furnaces for the extraction of zinc; zinc fume, or poussière, is pulverulent metallic zinc, which generally contains certain amounts—8 to 10 per cent.—of oxide of zinc, as also cadmium, arsenic, antimony, lead and other substances volatilised from the charge of the zinc distillation furnace. The zinc oxide mixed with it is produced by the action of air and moisture upon the finely divided metallic zinc at the commencement of the process of distillation. This zinc fume is found in the adapters, nozzles and other condensing arrangements of the distillation furnace. It is generally added to the charge of the distillation furnace in such proportion that its impurities may be distributed over large quantities of zinc, and thus have a less injurious effect upon the properties of the metal. On account of its easy reducibility, it is treated in those vessels which are least exposed to the action of heat. If zinc fume is treated by itself in distillation furnaces, zinc of an inferior quality is obtained, which is either mixed in with large quantities of pure zinc, or is sent into the market as zinc of an inferior quality. In this case the zinc fume is charged either into the less strongly heated vessels in the distillation furnace—that is to say, in the case of Silesian furnaces with several tiers of muffles into the lowermost muffles, or in the case of single Belgian furnaces into the topmost tier—or else it is treated when considerable quantities have accumulated by itself in ordinary distillation furnaces, the vessels in which, in this case, are charged for a certain time with zinc fume alone.

According to Massart,<sup>1</sup> at the works of the Nouvelle Montagne at Engis, in Belgium, there were produced during a 38 day campaign of the distillation furnaces from 43 tons 16 cwts. of zinc fume, containing 81 per cent. of zinc, 33 tons 14½ cwts. of crude zinc, with a loss of zinc of 5 per cent., and a consumption of 3,220 cubic feet of coal for fuel, and 537 cubic feet for reduction. The furnace treated 24 cwts. of zinc fume and 14 cubic feet of coal in 24 hours. Before charging the furnace was cooled down to a dull red heat; during the distillation the fire was kept moderately low in order to prevent

<sup>1</sup> *Rev. Univers. des Mines*, vol. xix., p. 201.

the charge from becoming pasty, as happens when the temperature is higher. The condensed zinc was removed seven times per day from the adapters; in order to prevent zinc from running out from the adapters, the nozzles had to be removed from the latter, and they were plugged by means of clay. A special method of extracting zinc from zinc fume, which has, however, been given up at the present day at most zinc works, consists in melting the zinc out of the fume in the so-called Montefiore furnace. This can be done by pressing together at a moderately high temperature the separate fluid particles of zinc, when they unite to a fluid mass, only retaining small quantities of oxide of zinc, whilst the greater portion of the

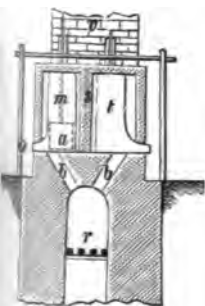


FIG. 202.

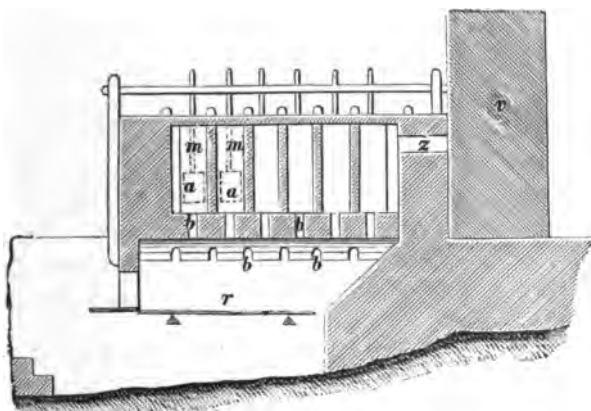


FIG. 203.

oxide is separated out. The melting is performed in furnaces containing two rows of vertical muffles made in the shape of a boot open at the toes. After the zinc fume has been charged, a clay piston attached to an iron rod is inserted into the leg of the boot. By the pressure of this piston upon the heated zinc fume, fluid zinc is expressed from it, and flows out through the openings at the toe of the boot. The constructions of these furnaces, known as the Montefiore furnace, after their inventor, is shown in Figs. 202 and 203, in which *t* are the clay boots, which are disposed in two rows in the interior of the furnace, and separated by the partition wall *s*. These boots are  $28\frac{3}{4}$  inches high, 7.2 inches inside, and  $9\frac{1}{4}$  inches outside diameter. The heating chamber is 6 feet 8 inches long, 3 feet 5 inches broad, and  $28\frac{3}{4}$  inches high; *a* are the movable clay pistons  $8\frac{1}{4}$  inches high and  $6\frac{3}{4}$  inches in diameter, and *m* are the iron rods to which they are attached; *o* are the openings through which the

zinc runs out or can be tapped out from the boots;  $r$  is the grate 5 feet 8 inches long and  $18\frac{1}{2}$  inches wide, from which the flame enters the furnace chamber through openings  $b$ , 3 inches wide, and after having surrounded the boots, escapes through the flue  $z$  into the stack  $v$ . At the Silesia Works in Upper Silesia a furnace was heated, not by a separate grate, but by the spare heat of the zinc distillation furnaces. The number of boots in a furnace varied from 8 to 12, there being 12 in the Figure shown above. The charge for a boot amounts to about 44 lbs. of zinc fume. After heating for three hours, the zinc will be in the fluid condition. Pressure is now applied, whereby the zinc is collected in the bottom of the boot and can be tapped out through the above-named openings. At Corphalie in Belgium, a furnace of this kind treated from 14 to 18 cwts. of zinc fume in 12 hours, with a consumption of 116 to 155 cubic feet of fuel, and a zinc extraction equal to 85 to 86 per cent. At the Silesia Works, the output of zinc in Montefiore furnaces heated by waste heat amounted to 85 to 86 per cent. Zinc obtained from the Montefiore furnaces is exceedingly brittle in consequence of the amount of zinc oxide which it contains. For this reason the treatment of zinc fume in these furnaces has been given up in most works in favour of its treatment together with zinc ores in the distillation furnaces.

Zinciferous flue dust is also added to the charges. Should it, however, contain considerable quantities of lead, it may be treated with sulphuric acid in order to obtain the zinc in solution in the form of white vitriol, whilst the leady residue is smelted for lead. This method is adopted at the Julius and Sophia Works in Goslar. Zinc-bearing flue dust from the blast furnaces in Upper Silesia contained: <sup>1</sup>—

	I.		II.
Silica . . . . .	23·64	. . .	25·98
Zinc oxide . . . . .	28·22	. . .	21·37
Lead oxide . . . . .	8·72	. . .	6·55
Ferrous oxide . . . . .	22·96	. . .	26·60
Ferric oxide . . . . .	trace	. . .	—
Alumina . . . . .	0·30	. . .	0·62
Manganous oxide . . . . .	2·58	. . .	3·58
Lime . . . . .	trace	. . .	—
Sulphur trioxide . . . . .	0·49	. . .	0·70
Sulphur . . . . .	0·52	. . .	0·26
Chlorine . . . . .	0·02	. . .	0·07
Carbon . . . . .	11·68	. . .	13·79

The residues from the adapters of the distillation vessels as also the residues from the Montefiore furnaces, which consist essentially

<sup>1</sup> Jensch. *Zeitschr. angew. Chem.*, 1890, p. 14.

of zinc oxide, are either added to the charges in the ordinary distillation furnace, or else treated by themselves in the topmost tiers of retorts in Belgian furnaces.

Fragments of adapters which have become saturated with zinc, gave the following figures on analysis. (Jensch. *Op Cit.*, p. 213.)

Zinc . . . . .	76.41
Lead . . . . .	0.39
Cadmium . . . . .	0.13

They are added to the ore charges.

Residues from the retorts and muffles contain 3 to 5 per cent. of zinc. The average composition of these residues from different Belgian works (numbered in the table) is given by Firket<sup>1</sup> for the year 1898 as shown on the following page.

Besides zinc the residues thus contain lead, iron, lime, magnesia, slag and the greater part of the coal used for reduction. Attempts have been made to wash these residues in order to obtain the zinc and coal, but without good results. The coal cannot be separated from the flaky slag mixed with it, and only small quantities of zinc-bearing mixtures containing 10 per cent. of zinc can be obtained.<sup>2</sup> The residues are accordingly thrown away, or put to such uses as the preparation of mortar or road metal.

Furnace calamine is also added in suitable proportions to the ore charge, after having been broken small. The composition of furnace calamine from the upper Silesian blast-furnaces, is given by Jensch<sup>3</sup> as follows:—

Carbon . . . . .	2.02	Magnesia . . . . .	0.08
Silica . . . . .	12.34	Phosphoric acid . . . . .	0.16
Ferrous oxide . . . . .	14.82	Sulphur . . . . .	0.12
Manganous oxide . . . . .	4.17	Sulphuric acid . . . . .	0.38
Alumina . . . . .	1.26	Zinc oxide . . . . .	59.42
Lime . . . . .	0.10	Lead oxide . . . . .	3.93

Skimmings rich in zinc are treated in the same way, or are distilled together with zinc fume and the residues from adapters and vessels.

Calcined silver ores rich in zinc are treated in the same way as calcined zinc ores.

Alloys of zinc with lead and silver or gold are obtained when silver is extracted from work-lead by means of zinc. The zinc is recovered from these alloys by heating it to above the boiling point

<sup>1</sup> *Annales des Mines de Belgique*, 1901, vi. (i and ii).

<sup>2</sup> *Steger, op. cit.* p. 54.

<sup>3</sup> *Zeitschr. f. angew. Chem.*, 1900, p. 14.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	IX.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Zinc . . . . .	4.00	2.50	3.7	2.3	?	?	2.60	3.84	4.0	3.40
Lead . . . . .	5.00	8.50	1.26	9	11.50	9.12	2.13	11.60	10.00	8.10
Iron . . . . .	16.55	14.50	?	?	?	15.65	15.72	11.19	?	?
Silver . . . . .	0.016	?	?	?	?	0.017	—	0.035	0.01	0.05
Copper . . . . .	0.05	?	?	?	?	?	—	0.19	—	?
Cadmium . . . . .	—	?	?	?	?	?	—	—	—	?
Arsenic . . . . .	—	?	?	?	?	?	—	—	—	?
Antimony . . . . .	—	?	?	?	?	?	—	—	—	?
Sulphur . . . . .	?	4.00	?	?	?	?	0.62	1.72	?	2.10
Lime . . . . .	2.50	2.50	?	?	?	7.10	4.00	1.33	8.00	?
Magnesia . . . . .	0.45	1.50	?	?	?	1.20	2.16	0.73	?	?
Silica . . . . .							34.30	32.23	17.50	?
Carbon . . . . .	50.00	60.00	?	?	?	41.60	30.02	30.40	?	?
Alumina . . . . .							2.60	1.10	?	?

of zinc in retorts made of a mixture of clay and graphite, and by collecting the volatilised zinc in adapters. This method of zinc extraction has been fully explained under the head of the extraction of silver by means of zinc.

### *Products of the Reduction Process*

The products obtained in the processes of reduction are zinc, zinc fume, and residues from the adapters and distillation vessels.

Zinc prepared at most works is impure, containing lead, iron, and other foreign bodies. The following table gives the percentage composition of different kinds of crude zinc.<sup>1</sup>

	I.	II.	III.	IV.	V.
Zinc . . . . .	97·41	98·05	99·39	99·98	99·28
Lead . . . . .	2·29	1·56	0·50	—	0·63
Iron . . . . .	0·13	0·10	0·04	0·02	0·05
Cadmium . . . . .	trace	0·28	0·28	—	0·05
Copper . . . . .	—	—	—	—	trace
Silver . . . . .	—	—	—	—	"
Sulphur . . . . .	—	—	—	—	"

In this table, I. represents Silesian zinc for the year 1871, II. Bleiberg zinc for the same year, III. zinc from La Salle (1871), IV. zinc from Pennsylvania, and V. zinc from Sagor in Carniola (1885).

In the next table are given analyses of zinc from the Paul Works in Upper Silesia, the metal being prepared in I. from blende alone, in II. from calamine alone, and in III. and IV. from a mixture of 75 per cent. of calamine and 25 per cent. of blende.

	I.	II.	III.	IV.
Zinc . . . . .	98·59	98·45	98·44	98·18
Lead . . . . .	1·32	1·49	1·47	1·70
Iron . . . . .	0·05	0·03	0·03	0·06
Cadmium . . . . .	0·03	0·02	0·05	0·06
Arsenic . . . . .	trace	0·002	trace	trace
Silver . . . . .	—	0·002	—	—

The following analyses are given by Jensch of crude zinc from the Rosamund Works in Upper Silesia (I. and II.) and

<sup>1</sup> Steger, *op. cit.* p. 76.

from other works in the same locality (III. and IV.—United Silesian zinc).

	I.	II.	III.	IV.
Zinc . . . . .	99·12	98·29	97·33	98·36
Lead . . . . .	1·85	1·67	2·61	1·52
Iron . . . . .	0·02	0·02	0·03	0·09
Cadmium . . . . .	0·003	0·004	0·02	0·01
Arsenic . . . . .	—	—	0·001	0·002
Residue (Carbon) . . . . .	0·001	0·005	—	—

Zinc prepared from flue dust at the Paul Works near Schoppinitz contained (in addition to other impurities):—

	I.	II.	III.
Zinc . . . . .	97·24	98·14	97·53
Lead . . . . .	2·17	1·74	2·41
Iron . . . . .	0·05	0·04	0·03
Cadmium . . . . .	0·53	0·07	0·03
Arsenic . . . . .	trace	—	—

Zinc from the Birkengang Works, Stolberg, contained 1·46 per cent. of lead and 0·02 per cent. of iron. In the next table are given analyses of zinc from various American works; I. and II. from the South West Missouri Works (analyses by Pack), III. from Lehigh, and IV. from the Passaic Works, New Jersey; and V. from Bethlehem, Pennsylvania.

	I.	II.	III.	IV.	V.
Zinc . . . . .	—	—	99·39	—	—
Lead . . . . .	0·07	0·006	—	0·03	—
Iron . . . . .	0·72	0·28	0·04	0·02	0·04
Cadmium . . . . .	—	—	0·08	—	—
Copper . . . . .	0·11	0·001	0·53	—	—
Silicon . . . . .	0·03	0·14	—	—	0·24
Arsenic . . . . .	0·06	0·06	—	—	—
Antimony . . . . .	0·02	—	—	—	—
Sulphur . . . . .	0·003	0·07	—	—	—
Carbon . . . . .	0·18	0·001	—	—	—

Zinc from Cilli, in Styria, contained 0·32 per cent. of lead and 0·025 per cent. of iron; that from Johannisthal, Carniola, contained 0·53 per cent. of lead, 0·07 of cadmium and 0·02 of iron.



The purest zinc is "Bertha Spelter," which is prepared at Pulaski in the United States from ores containing:—

Zinc oxide . . . . .	47·61	Calcium carbonate . . .	4·54
Silica . . . . .	29·37	Magnesium carbonate . .	2·07
Iron and Aluminium Oxide	9·23	Water . . . . .	8·23

This zinc contains 99·98 per cent. of zinc, 0·02 per cent. of iron, and only traces of lead and sulphur.<sup>1</sup>

Zinc fume contains zinc oxide, cadmium, lead, arsenic, antimony and any other volatile matter that may be present in the distillation charges. The amount of zinc oxides varies greatly, according to whether the zinc vapours have burned or not, and to whether the fume has been exposed for a long or a short time to the air, for air oxidises finely divided zinc. The following table gives analyses of zinc fume from various sources: I. from Borbeck (near Essen), II. from the Carondelet Works (Missouri), III. from the Theresa Works, Upper Silesia (the first fume that is formed),<sup>2</sup> and IV. is the average fume from the Silesia Works, Upper Silesia.<sup>3</sup>

	Zn.	ZnO.	Pb.	Cd.	As.	Insoluble residue.	Fe.	Cu.
I. . . . .	97·82	—	0·23	0·08		—	0·16	—
II. . . . .	29·89	57·74	trace	—	0·32	9·60	2·05	trace
III. . . . .	80·00	8·83	2·02	1·65	—	1·02	—	—
IV. . . . .	84·46	4·88	4·27	2·65	—	0·12	—	—
	C.	Sb.	S.	Fe <sub>3</sub> O <sub>4</sub>	Al.	Mn.	CaO.	MgO.
I. . . . .	—	—	—	—	—	—	—	—
II. . . . .	1·22	0·37	0·02	—	—	—	—	—
III. . . . .	0·23	—	—	1·02	0·20	1·81	2·80	0·67
IV. . . . .	—	—	—	0·90	—	—	2·46	0·24

Further analyses of zinc fume are given in the next table (quoted from Kosmann, *op. cit.*), I. is fume from the collecting chambers at Lipine, II. from the Giesche Works in Upper Silesia, the fume being obtained from chambers which are connected with Kleemann adapters. III., IV., and V., are from the flues at Paul Works, Schoppnitz,

<sup>1</sup> Moxham, *Eng. and Min. Journ.*, November 25, 1893.

<sup>2</sup> Kosmann, *Preuss. Minist. Zeits.*, 1883, p. 234.

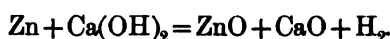
<sup>3</sup> *Ibid.*

and are samples of dust precipitated from the burning retort gases; VI. and VII. are later determinations of the same.

	I.	II.	III.	IV.	V.	VI.	VII.
Zinc oxide . . . .	54.45	88.20	65.71	78.15	83.95	89.92	90.45
Cadmium oxide . . .	3.62	1.46	7.11	2.09	1.68	3.21	2.76
Lead oxide . . . .	12.34	4.44	3.7	4.29	3.96	0.86	1.38
Sulphur trioxide . .	3.85	4.12	—	—	—	0.30	0.18
Iron oxide . . . .	25.72	1.50	{ 0.50	3.87	0.80	2.10	1.22
Insoluble . . . .			{ 1.98	3.45	1.16	0.55	0.42
Carbon dioxide . . .	—	—	—	—	—	2.44	3.20
Loss on ignition . .	—	—	20.42	6.56	8.71	—	—

The fume from Dagner's adapters, which is precipitated by water sprays on the way to the stack, contains, according to Steger<sup>1</sup>:—Zinc oxide 66—94 per cent., cadmium oxide 1.68—7.11, lead oxide 3.70—4.29, ferric oxide 0.50—3.87, and sand 1.16—3.45 per cent.

Zinc fume is worked up as described on p. 214. If it contains cadmium, it is used for the extraction of this metal. As "zinc grey" it serves as a paint, especially suited for iron work. It is also extensively applied in works and laboratories as a reducing agent for indigo, nitrobenzene, nitric acid, &c., and for preparing hydrogen by heating it with slaked lime. The equation for the last reaction is,<sup>2</sup>



### *Refining of Zinc*

Zinc as raked or tapped out of adapters, or as removed in the form of solid zinc from the collecting chambers of the old Silesian furnaces, is but rarely pure. It generally contains considerable quantities of lead and iron, together with mechanically enclosed impurities. The lead content may exceed 3 per cent., the iron is seldom over 0.2 per cent. As large quantities of lead diminish its extensibility, zinc which is intended for rolling must be freed as far as possible from it. This zinc, known as work-zinc or crude zinc, cannot be refined by an oxidising fusion, as is done in the case of silver, copper and lead, on account of the great affinity of zinc for oxygen. It may, however, be purified by slow remelting and allowing it to stand for a considerable time in the molten state. Under these circumstances the mechanically enclosed impurities which are lighter than zinc come

<sup>1</sup> *Zeits. d. Oberschl. Berg- und Hüttenm. Ver.*, 1885, p. 222.

<sup>2</sup> *Schwarz. Ber- d. deut. Chem., Gesellschaft*, 1886, 19, 1140.

to the surface, and can be removed as skimmings, together with a portion of the zinc oxide formed, whilst lead, as far as it is not alloyed with the zinc, and some iron, settle to the bottom in consequence of their higher specific gravities. The purified zinc can be ladled off from above the lowest portion of the bath of metal which contains the lead and iron, or this bottom part can be removed from the bath by means of an archimedean screw.

According to the temperature zinc will take up different quantities of lead; Roessler and Edelmann found that it will take up 5.6 per cent. at 650° C., whilst it takes up only 1.5 per cent. at its melting point. The latter amount cannot therefore be removed from the zinc by allowing it to settle. As most zinc ores contain lead, zinc containing a certain amount of lead will thus always be obtained in spite of refining. Only a small quantity relatively of iron can be removed from zinc by refining. Upper Silesian crude zinc, which seldom contains more than 0.1 per cent. of iron, still holds 0.02 to 0.03 per cent. after refining; refined Freiberg zinc contains 0.04 per cent. of iron. Refined zinc is thus a zinc-lead alloy with 1 per cent. of lead on the average, and the lead separated during refining contains a certain quantity of zinc. At the Paul works in Upper Silesia, the lead-zinc alloy separating out in the refining furnace, contains 95.76 per cent. of lead, 4.24 of zinc, 0.0008 of iron and a trace of cadmium. The iron collects after a time in a layer of zinc between the lead and the refined zinc, and forms what is called "hard zinc." Work-zinc obtained in the solid state, as used to be the case with the English zinc furnaces and the old Silesian zinc furnaces, had to be remelted in order to cast it into moulds. During this remelting, which was performed in pans made of cast-iron or clay, the impurities in the zinc separated out. To promote this operation, the molten zinc was stirred from time to time. The skimmings (zinc ash), which formed upon the surface of the bath of metal, and which consisted of a mixture of the separated mechanical impurities with oxide of zinc and metallic zinc, were removed by means of a perforated ladle. The zinc was finally cast into iron moulds, whilst the bottom portion of the metallic bath, which was rich in lead, was ladled out separately. Cast-iron pans were open to the objection that they contaminated the zinc with iron, and thus made it brittle. At present reverberatory furnaces with clay hearths are used for the refining of zinc, as is done, for example, at the larger works of Upper Silesia, the zinc in which contains 1.75 to 2.5 per cent. of lead. The construction of such a furnace is shown in Figs. 204 and 205.<sup>1</sup> The inclined hollowed hearth is made

<sup>1</sup> *Berg. und Hüttenm. Ztg.*, 1873, p. 290.

of lean clay rammed upon the brickwork of the furnace, and terminates in a sump *f*; *g* is the charging door through which the zinc which is to be melted, is introduced into the furnace; *h, h* are the fire-grates; *i* is an opening through which the purified zinc is ladled out. The flame traverses the furnace longitudinally and rises above the sump, passing thence to the stack. The waste heat is generally utilised for warming the chambers in which the zinc that is to be rolled, is heated. Another form of furnace provided with only one grate is shown in Fig. 206. *R* is the grate, *s* is the bed of fire-clay, *t* is the sump, *u* is the door through which the metal is ladled out, *v*

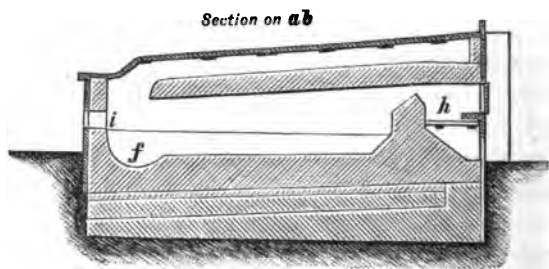


FIG. 204.

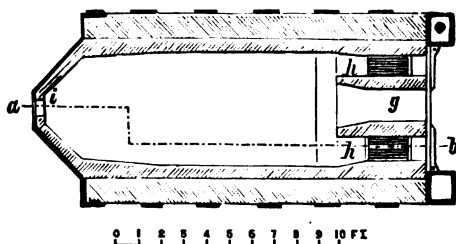


FIG. 205.

is the flue, *u* are chambers heated by the flame, in which zinc bars and sheets can be heated; *k* is a flue leading to the stack. At the flue end of the furnace there is a partition wall descending into the bath of metal in order to keep the air away from the latter. The opening for the introduction of the zinc into the furnace is at one side of the fire-bridge in a longer side of the furnace. The hearth is 15 feet 5 inches long and 6 feet 6 inches wide; the lowest point of the hearth is 1 foot 8 inches below the door out of which the metal is ladled. Such a furnace usually contains from 28 to 30 tons of zinc, and is capable of refining 9 to 10 tons in 24 hours, with a consumption of 18 cwt. of coal. A furnace similar to that first described.

at the Hohenlohe Works, near Kattowitz, such as is used in most of the works in Upper Silesia, is shown in Figs. 207 to 209, 207 being a longitudinal section, 208 a horizontal section, and 209 a cross section of the furnace, the length of which is 19 feet 8 inches and its width 10 feet 6 inches;  $r, r$  are the two grates; between them is the flue  $k$ , inclining towards the hearth, in which the zinc to be refined is charged. From this it flows, as soon as it is melted, down the inclined surface of the hearth, to the sump  $s$ . The flame traverses the furnace lengthways from the grate and escapes through openings,  $o$ , in the roof of the furnace, into flues leading to the stack  $E$ . Such a furnace will contain 30 tons of zinc.<sup>1</sup>

In order to avoid oxidation the zinc must be melted at the lowest possible temperature, and very gradually, whilst the flame is

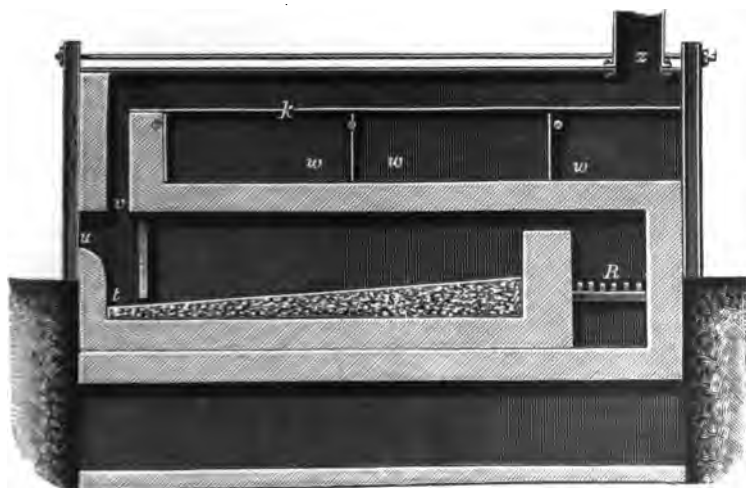
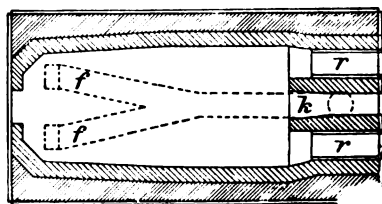
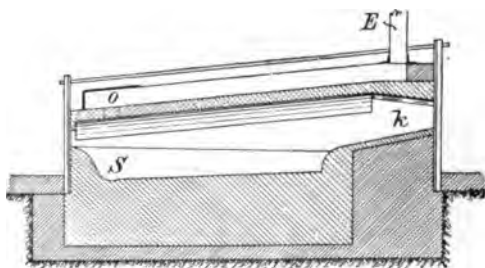


FIG. 206.

kept as reducing as possible. When the furnace has received its full charge of molten zinc—20 to 30 tons of zinc—which takes place after two or three days, the ladling out of the metal commences, as much fresh zinc being charged in as is ladled out, say 9 to 10 tons in 24 hours. From the metal bath, which is thus kept at a constant level, the lead is first deposited, followed by the iron, which forms with the zinc and a portion of the lead a difficultly fusible alloy, whilst the zinc forms the topmost layer. By means of a suitable tool, the pure zinc, the hard zinc, and the lead are easily distinguishable from each other. If an iron rod is slowly lowered into the metallic

<sup>1</sup> U.S. Pat. No. 702526, June 17, 1902.

bath in the furnace, the mass feels soft as far as the molten zinc extends; when the bar is forced further in, the mass feels hard, somewhat like ice at its melting-point. This is the layer of hard zinc. Below this the soft layer of molten lead is reached. The mechanical impurities, which have a lower specific gravity than the zinc, separate out upon the surface. After the zinc has been skimmed, it is ladled out from the bath in cast-iron ladles made as thin as possible, and is cast into moulds in the form of bars; in this form it is known in the trade as *Spelter*. If the zinc is to be rolled, these bars must be kept heated up to  $130^{\circ}$  C. When properly worked, the quantity of skimmings does not exceed  $1\frac{1}{2}$  per



FIGS. 207 and 208.

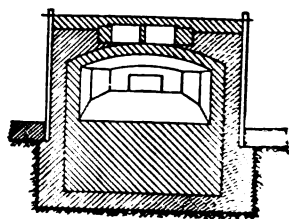


FIG. 209.

cent. of the zinc charge. If the temperature is too high, a mixture of zinc oxide and fluid zinc known as *burnt zinc* forms upon the surface of the bath of metal. For the removal of antimony and arsenic from the zinc, L'hôte<sup>1</sup> proposes the addition of chloride of magnesium during the fusion, which is said to remove the above metals in the form of chlorides. Richards<sup>2</sup> recommends the addition of aluminium to the molten metal for the purpose of separating the impurities from the zinc. He claims that by this means the impurities, with the exception of lead, separate out at the surface.

From time to time, the bottom layer of zinc containing lead and iron, which has accumulated in the sump, must be removed from the

<sup>1</sup> *Comptes. rendus*, 98. p. 1491.

<sup>2</sup> American Pat. 448802.

latter. In this case, the whole of the zinc in the furnace is first ladled out, and then the impure bottom zinc removed, or else the bath of metal is left in the furnace, and the zinc at the bottom is drawn out by means of a tube provided with an archimedean screw, or by means of an iron cylinder with a hole in the bottom, or again by means of an open clay tube, the bottom edge of which is notched, and which is inserted in the furnace before the commencement of the operation. The latter method allows the refining process to be carried on continuously, and is preferable to the two former. The first-named piece of apparatus consists of an iron tube or casing 4 feet 3 inches to 4 feet 7 inches long, and 4 feet in diameter, in which an archimedean spiral works. This tube is provided at its upper end with a spout through which the molten metal flows off, whilst the bottom end rests upon feet, the spiral being turned by means of a crank. The apparatus is inserted through openings, left for that purpose in the furnace, into the sump, and the handle is turned, whereupon the bottom layer of zinc rises in the tube and flows out through the spout; this apparatus is employed, for example, at Lipine. The second-named piece of apparatus consists of a cylinder with a hole in the bottom, this hole being plugged with clay. If the cylinder is lowered into the sump, and the hole in the bottom then opened, the impure zinc at the bottom rises into the interior of the cylinder and can be ladled out of it. The third piece of apparatus consists of a bottomless tube of fire-clay, the lower edge of which is notched. It is placed in the furnace before the leady zinc commences to separate, and is left in it during the whole course of the operations. The impure zinc passes into the tube through the notches and is ladled out from it as soon as it reaches a certain height. This apparatus is in use, for example, at the Paul and Wilhelmina Works in Upper Silesia.

The hard zinc is occasionally removed from the furnace, for instance when the furnace is shut down or repaired. The refined zinc is ladled out in these cases, the lead is removed from beneath the layer of hard zinc, by one of the methods just described, and finally the pasty mass of hard zinc is ladled out with a perforated ladle, which allows the lead still present to run away free from the hard zinc.

The consumption of coal in refining amounts to  $7\frac{1}{2}$  to 10 per cent. of the weight of the zinc melted. At Lipine, 9 tons of crude zinc, containing  $2\frac{1}{2}$  per cent. of lead, are melted in 24 hours, refined zinc with 0.5 per cent. of lead being produced. At the Hohenlohe Works 10 tons are melted in 24 hours, or 5 tons every 12 hours,

containing 3 to 4 per cent. of lead, the refined zinc containing 98·87 per cent. of zinc, 1·07 per cent. of lead, 0·02 per cent. of iron, and 0·04 per cent. of sulphur.

Refined zinc from the Paul Works in Upper Silesia had the following composition:<sup>1</sup>—

	I.	II.	III.	IV.
Zinc . . . . .	98·72	98·93	98·77	98·85
Lead . . . . .	1·12	1·00	1·18	1·10
Cadmium . . . . .	0·01	0·02	0·03	0·02
Iron . . . . .	0·02	0·03	0·02	0·03
Antimony . . . . .	0·02	—	—	—
Thallium . . . . .	—	0·01	—	—

In the following table are analyses of refined zinc from the Beuthen Works, Morgenroth (I. and II., Jensch), from the Lazy Works, near Beuthen (III., Steger), and from Freiberg (IV., Föhr).

	I.	II.	III.	IV.
Zinc . . . . .	98·87	98·92	—	—
Lead . . . . .	1·11	1·06	1·12	1·03
Cadmium . . . . .	0·001	0·002	0·017	—
Arsenic . . . . .	—	—	0·02	trace
Iron . . . . .	0·02	0·02	0·02	0·04
Tin . . . . .	—	—	—	0·07
Carbon . . . . .	0·001	0·001	—	—

Hard zinc, which contains much lead and iron, is either distilled or sold to silver works where argentiferous lead is treated for silver. Attempts have been made to treat it electrolytically.

Zinc direct from the retorts can be refined in Herter's apparatus without the need for re-melting. This apparatus consists of a ladle on trunnions, transportable or suspended from a crane, with a fire-proof lining and jacket, for the reception of the molten zinc. The vessel is heated by a grate situated within the jacket and the different layers of metal which are formed can be run off separately through a hole in the bottom of the vessel. Zinciferous lead settles to the bottom, and may be run off. Refined zinc can be removed either by tipping the apparatus, or by running off after the lead has been tapped. This apparatus is in use in Upper Silesia. I:

<sup>1</sup> Steger, *op. cit.* p. 78.



is represented in Fig. 210. The pan suspended from the crane is shown in Figs. 211 and 212, and the device for raising the pan in Figs. 213 and 214.

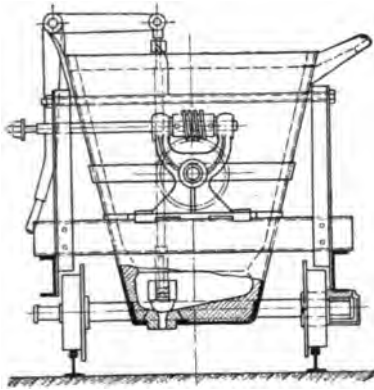


FIG. 210.

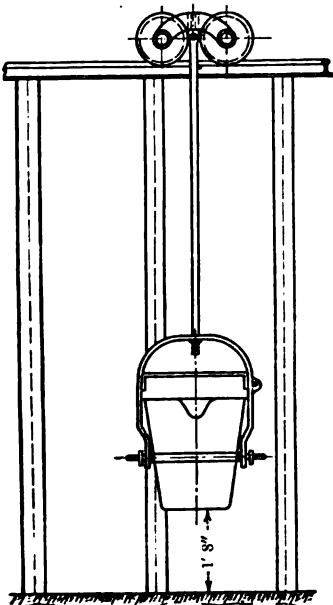


FIG. 211.

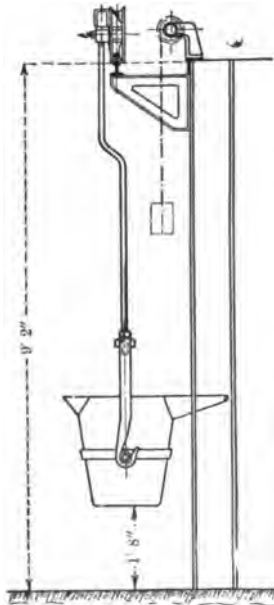


FIG. 212.

Zinc-bearing scums are added to the distillation charges. Up to 60 per cent. of their content can be liquated out, when sal-ammoniac is sprinkled over them before their removal from the

furnace, or by addition of 1 part of salammoniac to 400 parts of scums in the reverberatory furnace, after the zinc has been run off.

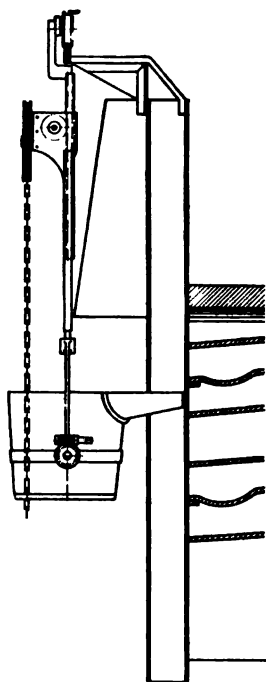


FIG. 213.

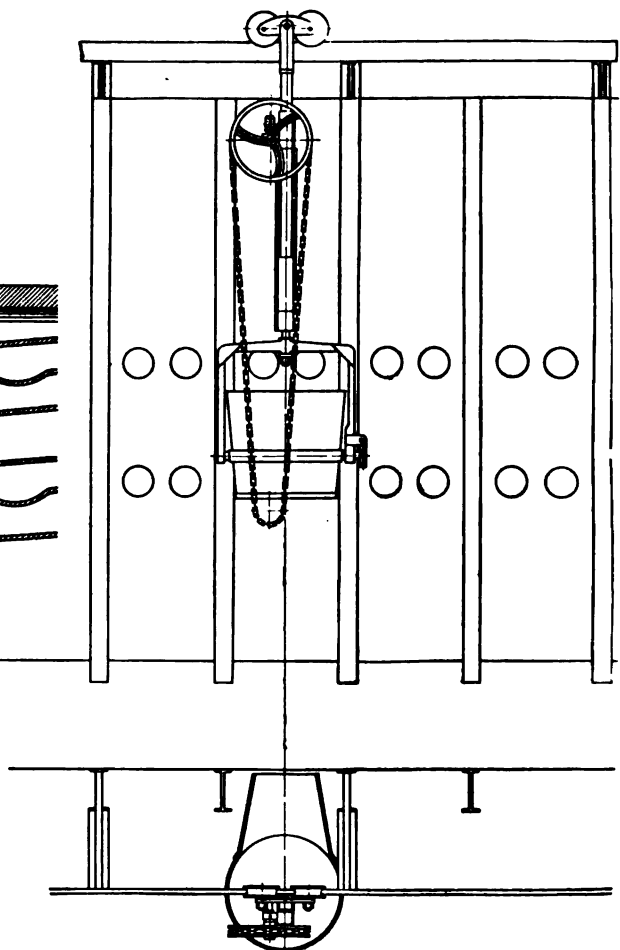


FIG. 214.

## EXPERIMENTS AND PROPOSALS FOR THE IMPROVEMENT OF THE DRY METHOD OF ZINC EXTRACTION

### *Extraction of Zinc in Shaft Furnaces*

Owing to the many shortcomings of the present method of the extraction, attempts have long been made to replace the process of



distillation in clay vessels by distillation in shaft furnaces. These attempts have, however, been fruitless as regards the production of solid zinc. It would be useless to describe fully the various methods and proposals which have been made in this direction, as, for example, those of Dyar, Rochaz, Shear, Duclos, Schmelzer, Swindell, Broomann, Lesoinne, Adrien,<sup>1</sup> Muller and Lancauchez,<sup>1</sup> Gillon,<sup>2</sup> Clerc,<sup>3</sup> Glaser,<sup>4</sup> Neuendahl, Walsh, Eichhorn, Westmann, Rigaud, Battrey, Kleemann and Sébillot.<sup>5</sup>

The whole of these have failed on account of the difficulty of condensing the vapours, as has been shown by the recent exhaustive experiments carried out by Hempel.<sup>6</sup> Zinc vapours, which are mixed with considerable quantities of neutral gases, cannot be condensed by cooling to fluid zinc, because the zinc separates in a pulverulent condition. When shaft furnaces are employed for the production of zinc, the products of combustion, carbon monoxide and nitrogen, are necessarily mixed with the carbon monoxide produced by the reduction of oxide of zinc and with the zinc vapours. These latter are, therefore, diluted to such a degree that, when cooled, they will no longer condense to a fluid, but remain in the form of a fine dust suspended in the gases. Even when strongly heated air is employed for burning the coke in shaft furnaces, no change is produced in the behaviour of the zinc vapours, as has been shown by Hempel. In the present condition of science and technology, all attempts at the production of zinc in shaft furnaces must, therefore, be looked upon as presenting no probability of success. The future will show whether it is possible to obtain liquid zinc profitably by the use of shaft furnaces, working under pressure and with electrical heating. The proposed methods for effecting this have not yet got beyond the experimental stage. Pulverulent zinc readily oxidises in contact with the air, and, therefore, always contains certain quantities of oxide of zinc, as is the case with the above described zinc fume. Moreover, the oxidation of a portion of the zinc by the carbon dioxide and water vapours present in the furnace is also inevitable. By the employment of excess of fuel, by taking care that the charges and fuels shall contain neither water nor carbon dioxide, by the employment of ores which are free from oxide of iron (the latter being reduced even in the upper half of the furnace by carbon monoxide, thus producing carbon dioxide), and by the employment of heated air,

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1862, p. 324.

<sup>2</sup> *Ibid.*, 1881, p. 6.

<sup>3</sup> *Ibid.*, 1887, p. 83.

<sup>4</sup> *Ibid.*, No. 48449.

<sup>5</sup> *Preuss. Zeitschr. für das Berg-, Hütten- und Salinenwesen*, 1900, p. 406.

<sup>6</sup> *Berg- und Hüttenm. Ztg.*, 1893, Nos. 41 and 42.

these objections can nevertheless be considerably limited, as is, indeed, also the case in the process of zinc distillation in smaller vessels.

Whilst it is thus impossible to produce solid zinc in shaft furnaces, it is nevertheless quite possible, as Hempel has shown, to produce zinc oxide in such a furnace and also pulverulent zinc containing only relatively small quantities of oxide. The shaft furnace, therefore, presents a means for producing bye-products rich in zinc for distillation in retorts. In this respect, especially as regards the formation of pulverulent zinc, it may be worth while to experiment further upon the shaft furnace. According to Hempel's experiments, by the use of hot blast it is possible to obtain zinc fume very rich in zinc in the shaft furnace, and to separate it by means of centrifugal machinery from the gases. This zinc fume can be compressed into a very small volume by pressure, and this protects it from oxidation; from the zinc dust so treated zinc can be obtained both by distillation, without the addition of carbon, and also by means of electrolysis. Hempel submitted the compressed zinc dust to distillation, without adding carbonaceous matter, and obtained two-thirds of the fume in the form of metallic zinc of great purity. The residue contained oxide of zinc together with lead, silver, copper, &c., combined with oxygen and sulphur, which had been volatilised, together with the zinc, in the shaft furnace. Hempel used *zinc-coke* for the shaft furnace charge, this material being produced by heating together 1 part of zinc oxide, 3 parts of coal, and 0.05 part of caustic lime in a retort, and allowing the caked mass to cool with the exclusion of air. The shaft furnace was provided with an iron stove for heating the blast, and was constructed like a Sefström furnace. The gases, together with the zinc vapours, passed from the throat of the blast furnace into an iron tube, in which they were cooled down to 30° C. The gases were drawn off from the furnace and the zinc fume separated from them by means of a centrifugal apparatus, the construction of which is shown in Figs. 215 and 216. It consists of a wheel, *A*, with 8 vanes, which is driven by means of the grooved pulley, *a*, driven by a steam engine, the velocity being from 1,000 to 3,000 revolutions per minute. The wheel rotates inside a casing, *B*, which is again contained in the larger cylinder, *C*. The casing was open below, but closed above. The cylinder, *C*, was closed below by means of a cone, and provided above with a removable cover, *b*. The gases and zinc vapour entered through the tube *c*; when it reached the interior of the machine, the dust was flung, by centrifugal action, against the projections of the casing

*B*, whence it dropped down into the conical portion of the cylinder *c*, where it was deposited and whence it could be removed by means of the spout *e*. The gases escaped through the tube *d*, and were made to traverse a bag in which the remainder of the zinc dust was retained, so that the gases escaping therefrom were perfectly free from fume. The proportion of carbon dioxide in the escaping gases, which, as is well known, decreases as the furnace temperature increases, and which amounts to under 1 per cent. at a white heat, had gone down to 0.7 per cent. before charging the zinc-coke furnace, and varied during the three hours that distillation lasted, between 1.8 and 4 per cent. of the gaseous mixture.

The zinc fume produced contained 72 to 90 per cent. of zinc. It is liable to oxidise rapidly in the air, and if charged in the pulverulent form into retorts or muffles for the purposes of distillation, would

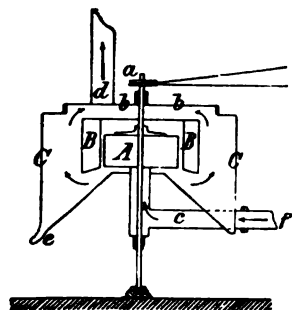


FIG. 215.

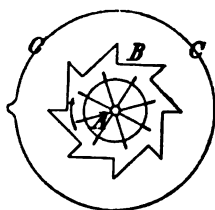


FIG. 216.

require the addition of carbon for the reduction of the zinc oxide, together with a very high temperature. In order to avoid this oxidation, it was compressed into blocks. According to the experiments of Hartig,<sup>1</sup> a pressure of 30 atmospheres reduced it to 13.3 per cent. of its original volume, 100 atmospheres to 10 per cent., and 200 atmospheres to 8.7 per cent. Accordingly, as a pressure of 100 atmospheres can easily be produced by means of screws, levers or hydraulic presses, there is no difficulty in compressing zinc fume to one-tenth of its original volume. Hempel obtained, by the distillation of this compressed zinc by itself, without any addition of carbon, two-thirds of the weight of the former in the form of very pure metallic zinc. In treating a charge to which ferric oxide and argenterous lead had been added, Hempel obtained zinc fume containing 80 per cent. of zinc, which contained the whole of the lead and silver. The iron was obtained in the form of white pig-iron; the

<sup>1</sup> *Loc. cit.*

slag left in the furnace contained 58·3 per cent. of silica, 10·4 per cent. of alumina, 8 per cent. of ferric oxide, 15 per cent. of lime, 1·0 per cent. of zinc and 1·8 per cent. of sulphur. This zinc dust was also compressed and distilled without any addition of carbonaceous matter. Two-thirds of its weight were obtained in the form of pure zinc, together with a residue having the following composition :—

SiO <sub>2</sub> . . . . .	41·6	Zn . . . . .	33·6
Fe <sub>2</sub> O <sub>3</sub> . . . . .	2·93	S . . . . .	8·1
CaO . . . . .	0·6	PbS and Ag <sub>2</sub> S . . . .	1·05

No experiments have been published with respect to the electrolysis of the compressed zinc dust. It could be moulded into soluble anodes, and as the zinc is chiefly present in the metallic form, a considerable quantity of electrical energy would be developed by its solution, so that only a low tension current would be required. In consequence of the above experiments Hempel proposed the extraction of zinc from ores which contained considerable quantities of zinc in addition to lead and silver, and which cannot be separated by dressing operations into zinc ores on the one hand and lead and silver ores on the other. The process is to comprise the following operations :—

1. The production of zinc fume in shaft furnaces.
2. The compression of the zinc fume produced.
3. The distillation or electrical refining of the compressed zinc fume.

The ore, after having first been calcined, has to be fritted, or, if coking coal is available, ground, without being fritted, with this coal, and then coked. If the ore is rich in iron, the iron must first be reduced, otherwise zinc vapours would be re-oxidised by the carbon dioxide produced in the upper part of the furnace, as occurs in iron blast-furnaces. The gases evolved from the furnaces, after having been freed from the zinc vapour, consist essentially of carbon monoxide and nitrogen, and are to be used for heating the blast or the distillation furnace, and for firing boilers. On escaping from the furnace, the gases are first passed into iron tubes kept cool by exposure to the air, in which the former are to be cooled down to 50° C., and simultaneously to deposit a portion of zinc fume; they then enter one, or a series of, centrifugal machines, which they traverse one after the other, in which nearly the whole of the zinc fume still retained is separated out. Hempel proposes the centrifugal machines shown in Figs. 217 to 218. *A* is the fan, *B* the casing, *C* the cylinder. The fan is driven from below. It would be best, as is customary with centrifugal machines, to support the fan in a movable bearing

with an india-rubber ring. If the speed of the fan for the separation of all the fume is found to be too high, it might be necessary to follow these machines by filters of sacking to separate out the last trace of zinc fume.

In order to avoid the formation of zinc oxide, the furnace should be so worked that the proportion of carbon dioxide in the escaping gases should not exceed 4 per cent. The compression of the zinc fume is to be performed in two operations. The first pressure is to be applied by means of a machine in which a spindle with a rapid pitch screw is quickly employed, so as to produce a pressure of 10 to 20 atmospheres, the final pressure being given by means of a hydraulic press. The distillation of the zinc dust, moulded into the form of cylinders, is to be carried out in retorts which are a trifle larger than the cylinders of zinc fume. These proposals of Hempel have not

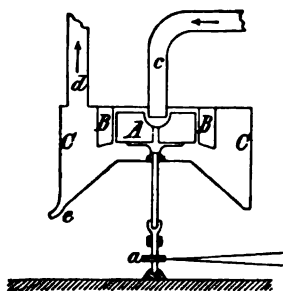


FIG. 217.

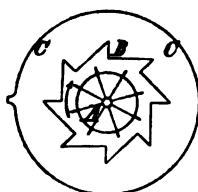


FIG. 218.

yet been carried out on a large scale. With ores carrying considerable quantities of lead and silver, difficulties may be met with in practice, as, on the one hand, fluid argentiferous lead and a considerable quantity of slag rich in zinc would be formed in the blast furnace, whilst, on the other hand, the zinc fume obtained would contain considerable quantities of lead, the treatment of which in retorts presents difficulties.

With regard to the production of zinc under pressure, Lungwitz<sup>1</sup> has proposed smelting the ores at such a pressure that liquid zinc is formed, the tension of zinc vapour at 1034° C. being less than 2 atmospheres according to Barns. The shaft furnace to be employed should be water jacketed and have a tightly closed top, and the inside of the furnace with its charge of ore and fuel should be under a pressure of 3 atmospheres. The zinc liberated under the conditions would be liquid and could be tapped from time to time. This process has not yet come into use.

<sup>1</sup> Ger. Pat. 83571.

Schuephaus<sup>1</sup> has described and carried out experiments with an electric furnace, holding cast iron crucibles lined with clay, for the reduction of zinc oxide under pressure. The reduction of the oxide of zinc begins at 910° C., and by heating the mixture of coal and zinc oxide to 1150° C. under a pressure of 2 atmospheres, liquid zinc collected at the bottom of the crucible. Nothing is known as to the application of this process.

The production of zinc oxide, or of a mixture of zinc and zinc oxide, in shaft furnaces presents no technical difficulties, if the formation of carbon dioxide by the combustion of the fuel is favoured by blowing an excess of air into the furnace, and, generally speaking, if an excess of air is present in the furnace. In the case of charges rich in iron, the formation of carbon dioxide is promoted by the fact that ferric oxide is reduced to metallic iron at a low red heat by carbon monoxide with the formation of carbon dioxide. In these cases, the zinc would be reduced in the lower part of the furnace by means of the carbon present. The excess of air, together with the carbon dioxide present in the upper part of the furnace, would again oxidise the vapours of zinc as they rise up. This takes place, for example when ores of iron, lead, copper or silver, containing zinc, are smelted in furnaces of comparatively small height. That the reduction of zinc takes place without any difficulty in these cases, is proved by the method to be presently explained for the production of zinc white direct from the ores. It is necessary to cool down the zinc fume and to separate it from the neutral gases by means of dust chambers and filtering appliances. Of the shaft furnaces that have been patented for the production of zinc oxide, not a single one, as far as the author knows, has been used practically. Zinc oxide intended for reduction has, up to the present, only been obtained as a bye-product when zinciferous ores such as franklinite are smelted in shaft furnaces, or when zinc white is produced in furnaces with Wetherill grates (see the production of zinc white).

As an example of a patented shaft furnace for the extraction of zinc oxide from ores, the furnace of Harmet may be mentioned, although it also has not been used practically.<sup>2</sup> The furnace, Fig. 219, has a closed top, *a*; by means of tuyeres, *T*<sup>1</sup>, *T*<sup>2</sup>, in the upper part of the furnace, as also by means of the tuyeres *T*, situated just above the bottom of the furnace, hot air is forced into the latter. The zinc reduced from the ores escapes in the form of vapour through the flues, *i*, into the chambers, *D*, where it is completely oxidised by means

<sup>1</sup> *Journ. Soc. Chem. Ind.*, November 30, 1899, p. 987.

<sup>2</sup> D.R.-P. No. 11197.



of cold and moist air entering through the tubes, *t*, and is then to be collected in the form of zinc oxide in chambers. The residue, free from zinc, is to be fused into a slag in front of the tuyere *T* and to run out of the furnace. For the production of metallic zinc, which is, however, subject to the above-named difficulties, the furnace is to be made higher. In this case, the zinc vapours are to be conducted, at a certain pressure which prevents the entrance of atmospheric air, through chambers filled with charcoal, and then passed into condensers. For the above-named reasons, here also zinc fume alone would be obtained. For the production of zinc oxide, furnaces with Wetherill grates are better suited than are shaft furnaces.

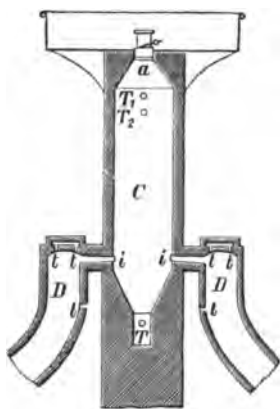


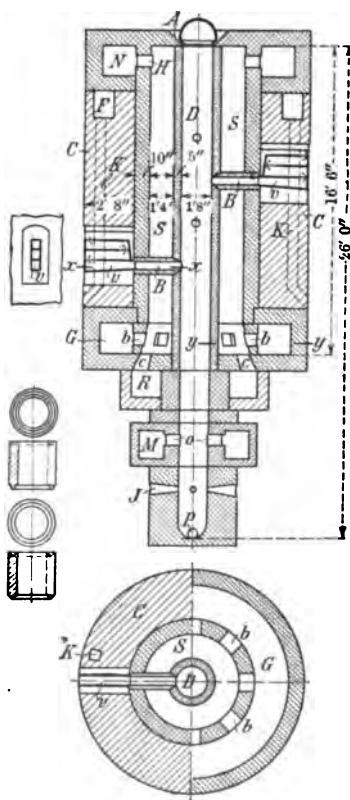
FIG. 219.

Biewend has proposed the blast furnace for the decomposition of zinc blende by means of iron.<sup>1</sup> The iron is to be added either in the metallic state or reduced from oxides charged for that purpose. The fuel and reducing agent for the oxide of iron is to be coke or charcoal. The zinc separated out in the gaseous form is to be conducted at a high temperature—800° C.—into condensers filled with red-hot coke or charcoal and condensed therein to the liquid state, whilst the sulphide of iron formed by the decomposition of the sulphide of zinc, and the slags produced from the ashes of the fuel and the impurities of the zinc blende, forming a silicate of lime and alumina, are to be tapped out of the furnace in the molten condition. The sulphide of iron can be converted into ferric oxide by calcination, and after being reduced can be used for the decomposition of fresh quantities of sulphide of zinc. The gases, freed from zinc in the condensers, and which consist of nitrogen and carbon monoxide, are to be used as fuel. The possibility of the decomposition of sulphide of zinc by iron in blast furnaces has been proved by the smelting of iron ores containing zinc blende. As, however, the zinc vapours formed are also diluted in this case by vapours of nitrogen and carbon monoxide, it is doubtful whether the zinc can be condensed to a liquid even by the employment of condensers filled with red-hot coal. That the condensation of zinc to a liquid may be possible to a certain degree, has been proved by the production of fluid zinc in the so-called *Zink stuhl*, in the old shaft furnaces of the lower Hartz, in which zinciferous

<sup>1</sup> D.R.-P. No. 81358, August 7, 1894.

lead ores were formerly smelted. If the condensation of zinc in the liquid state is not feasible, it would be necessary to be content with the production of rich bye-products. Hitherto no experiments have been tried on a large scale upon this process.

A furnace which is a combined muffle and shaft-furnace has been proposed by Schmieder (1903), and is represented in Figs. 220—223. *D* is the shaft or muffle made of carborundum the upper two thirds of which is enveloped with the hot gases. This, along with the annular



FIGS. 220—223

space *S*, into which producer gas and air are led, forms the crucible furnace. The producer gas passes from the generator into the circular flue *G*, and thence through the flues *b* into the chamber *S*. The air enters the same chamber from the flue *R* through the openings *C*. The products of combustion rise upwards and escape at the end of the chamber through the flues *H* into the main flue *N*, whence they are led to the stack. The material is charged through the hopper *A*, which can be closed down tightly, at the top of the muffle, and the zinc vapours and other gases escape through the pipe *B* into the condensers *V*, where the zinc is condensed. The gaseous products of reduction and the dust pass on through vertical flues *K* into the collecting flue *F*, and from this through precipitating boxes into the stack. The residues pass to the lower part of the muffle, or what may be called the shaft furnace, and are there subjected to a blast of air

which enters through the openings *J*, and which brings about the oxidation of any zinc retained in the residues. The zinc oxide thus formed is led through the openings *O* into the flue *M*, and thence through precipitation boxes into the stack. Part of the blast rises in the shaft and along with the carbon monoxide helps to dilute the zinc vapours. There are no details known as to the trials which have been carried out with this furnace.

Armstrong<sup>1</sup> has proposed a shaft furnace with boshes of circular horizontal section, in which is a second cylindrical shaft stretching from the boshes to the throat. The inner shaft holds the charge, and the annular space between the two shafts contains the fuel, the two combining at the boshes. Zinc vapours and the products of combustion are drawn off through holes at the bottom of the annular space, and are led through a bath of molten zinc, which condenses the zinc vapour, and allows the burnt gases to pass through. The zinc bath is in the form of a trough which surrounds the furnace; from this the zinc is tapped from time to time. The non-volatile metals and the slags formed from the gangue of the ores and the ashes of the fuel, collect in the crucible of the furnace, and are tapped occasionally. There is no information to hand as to the working of this furnace.

Another proposal of Armstrong<sup>2</sup> is to lead the zinc vapours and carbon monoxide from the furnace through a layer of glowing coke and from there through cooled pipes to a condenser. The object of this is to get the zinc in the pulverulent form in an atmosphere of carbon monoxide. The gases issue from the condenser through a trap closed with oil or some other suitable liquid, which retains the zinc dust; this is then collected and pressed, mixed with coal and subjected to distillation.

Nagel<sup>3</sup> proposes to reduce a mixture of ore and coal in a shaft furnace by blowing heated water-gas through the mixture. The object of the water gas is to reduce the zinc oxide, while the coal reduces the carbon dioxide and water produced in this reaction. The shaft furnace is similar to those used in smelting lead ores, and the water-gas is blown in through tuyeres situated one-third the way up the furnace. The zinc vapours are drawn off at the upper closed end of the furnace into a condenser, and the hydrogen and the carbon monoxide mixed with them are used in heating the water-gas. Under practical conditions of working, 1·5 tons of water-gas containing 1·4 tons of carbon monoxide and 0·1 ton of hydrogen, heated to 1000° C. and occupying 366,600 cubic feet, are said to suffice for the reduction of 8·1 tons of zinc oxide. Nothing is known about the working of this process.

#### *The Extraction of Zinc in Reverberatory Furnaces*

The extraction of zinc in reverberatory furnaces has been frequently attempted, but has always been attended with unfavourable results.

<sup>1</sup> Brit. Pat. No. 3462, February 21, 1900.

<sup>2</sup> *Ibid.* No. 11389, June 3, 1901.

In consequence of the oxidising action of the gases in these furnaces, zinc oxide was always obtained, but never the metal. Brackelsberg<sup>1</sup> attempts to avoid the oxidation of zinc by moulding a mixture of ground ore and coal into bricks, which he builds into columns in the laboratory chambers of reverberatory furnaces heated by producer gas, filling the interspaces between these columns by briquettes of coal or other carbonaceous fuel. The producer gas is to be burned by means of air introduced either by pressure or by draught. The flames are to pass through vertical spaces, left when the briquettes are built up, from above downwards, into a condensing chamber built below the laboratory chamber of the furnace, and thence into the gas producer of a second furnace. By means of the flames, these briquettes are to be heated to the temperature of reduction of the zinc, the excess of carbon in the furnace reducing the carbon dioxide to carbon monoxide. In the condensing chamber blocks of metal cooled by water and covered with fire-clay are distributed. The zinc is supposed to collect in the liquid form upon the bottom of this condenser and to be tapped off from time to time. Nothing is known up to the present as to the employment in practice of this furnace. Even though it might be possible to avoid the oxidation of the zinc, the zinc vapours would be diluted to a very great extent by the products of combustion of the producer gas and the nitrogen of the air, so that it would be impossible to count upon the production of liquid zinc. As in the case of the shaft furnace, zinc fume would be formed; the production of liquid zinc in reverberatory furnaces, must therefore be looked upon as hopeless, as only bye-products rich in zinc could be obtained in them.

Glaser<sup>2</sup> has proposed to produce zinc oxide in the reverberatory furnace by heating bricks, either solid or hollow, made by compressing zinc ores and coal with some binding material, up to the point of reduction of the oxide. The zinc vapours are then to be burnt by admitting air, and the dust collected in fume-chambers. This method seems feasible, but it requires pure ores for its execution.

M. Roux and J. Desmazures<sup>3</sup> propose to fuse zinc blende, containing silver-bearing galena, in a retort with litharge, air being excluded. The lead, carrying silver, collects at the bottom of the retort, and the zinciferous residues are heated with a flux, hot-air being blown through the molten mass. In this way the zinc oxide is said to separate out on the surface of the molten mass. Nothing is known concerning the application of this process.

<sup>1</sup> D.R.-P. No. 75090, August 27, 1893.

<sup>2</sup> Ger. Pat. 31716.

<sup>3</sup> Ger. Pat. 82097.

*Proposals for the Improvement of the Condensation of Zinc Vapours when the Distillation Process is carried on in Vessels*

As is well known, in the present method of zinc extraction the condensation of the vapours is the weakest point of the process. The greater part of the loss of zinc is due to the fact that a portion of the zinc vapours is never condensed at all, and that another portion, on account of its low tension as compared with atmospheric air, is not expelled from the retorts, but burns when the latter are emptied out. The condensation of zinc vapours is only complete between the narrow temperature limits of  $415^{\circ}$  and  $550^{\circ}$  C. If the temperature of the adapter, in which condensation takes place, is lower than  $415^{\circ}$ , the zinc passes from the condition of vapour direct to the solid state and forms a fine dust, which is in part carried off by the neutral gases. If the temperature exceeds  $550^{\circ}$  C., the zinc vapours escape without being condensed. Imperfect condensation is due to the impossibility of regulating the temperature of the small adapters at present in use, which, in consequence of their close connection with the furnace, necessarily fluctuates with every variation in the temperature of the furnace. Zinc vapours remain in the retorts at the end of the distillation, because on account of the present method of connecting retorts and adapters it is impossible to draw these vapours out of the retorts into the adapters by means of draught.

L. Lynen, of London,<sup>1</sup> has constructed a condensing chamber common to several adapters, which is to replace the present form of condenser and to avoid the above-named objections. Its arrangement is shown in Figs. 224 to 226. There are here two condensing chambers, *b*, about which four separate furnaces, separately fired, are so arranged that one condensing chamber lies between each pair of furnaces. The furnaces are fired with gas, and have three tiers of muffles, *a*, one above the other. These are luted to perforated bricks, *d*, which are so shaped that they connect the common condensing chamber with the back end of the muffle. The condenser has a sump, *e*, from which the zinc can be tapped off, and a bath of zinc of a definite depth is always left in the condenser to regulate the temperature. For the same purpose, there is a row of tubes, *c*, through which air can be admitted into the condenser and thus cool it if required. It is connected by means of the flue *f* with the dust flues *g*, and with a dust chamber in which any zinc fume formed is collected. From this dust chamber the current of gases

<sup>1</sup> *Zinc Distillation with a Common Condensing Chamber*, L. Lynen. London, 1893; August Siegle, 30 Lime Street.

passes into a stack connected with it. In consequence of the connection of retorts, condenser, dust chamber and stack, it is possible to draw any zinc vapour that may be left in the retort at the end of the distillation out of that retort by means of a light draught. The thickness of the walls of the condenser, the bath of zinc at the bottom, and the passage of air through the air tubes in case the condenser becomes overheated, are supposed to make it possible to keep the temperature of the condenser within the requisite

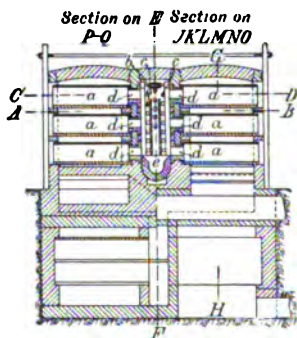


FIG. 224.

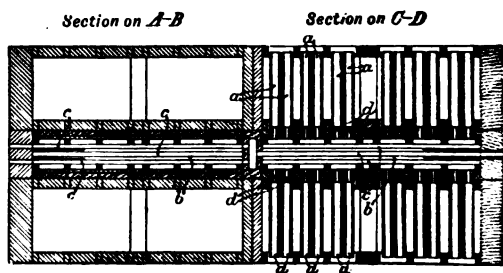


FIG. 225.

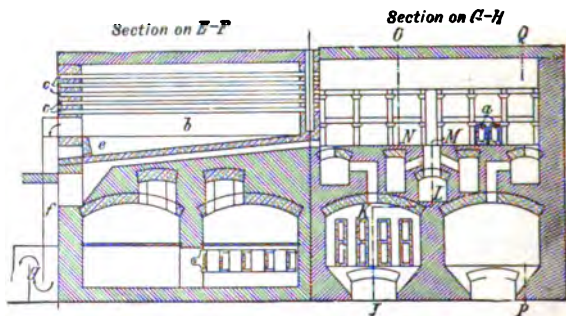


FIG. 226.

limits. The bath of zinc not only acts as a regulator, but promotes condensation by surface attraction. Finally, it also admits of the lead separating out in the lower portion of the sump and thus forms a partial refining furnace. When the distillation is finished, the system is to be worked with a gentle draught in order to draw out the last traces of zinc vapour from the retorts; as in this case air has to be admitted into the retorts, it is possible that a portion of the zinc vapours may be converted into fume. Nothing is known up to the present of any practical results obtained from these proposals of Lynen.

Biewend and the *Actiengesellschaft für Zinkindustrie* in Oberhausen<sup>1</sup> propose to condense the zinc vapours by leading them into chambers filled with lumps of charcoal, coke, quartz or asbestos, lengthening the path taken by the gas by means of suitable partitions in the chambers. The chambers are made with double iron walls between which air or water can circulate to promote cooling, and the gases can be made to pass through two neighbouring chambers, first in one direction, then in the opposite, by means of a reversing arrangement. In this way it is stated that a uniform temperature can be attained, and the formation of zinc dust can be prevented, though the latter is precipitated when the zinc vapours are much diluted with gases.

*Proposals for Improving the Material and Shape of the Vessels*

Richter and Lorenz<sup>2</sup> have suggested a rotating muffle furnace, that is, a horizontal sheet-iron cylinder lined with fire-proof material, and holding a retort in the middle. The retort is kept in place by projections from the cylinder, and the space between these projections serves for the passage of the hot gases from the grate. The cylinder with the retort and adapter is set in rotating or swinging motion by means of friction rollers. The pear-shaped adapter is connected with a condensing chamber. The charge occupies only one half of the retort space. The motion of the retort is supposed to effect a more thorough mixing of the charge and a shortening of the time of distillation. This furnace has not yet found practical application.

Steger<sup>3</sup> has proposed to replace clay, on account of its many defects, by magnesia and to build fixed muffles from tiles made of this material, which are to be much larger than the vessels at present employed for zinc distillation. According to his statements, magnesia conducts heat  $2\frac{1}{2}$  to 3 times as well as clay, is impenetrable by zinc vapours, is much stronger than clay, and resists higher temperatures. The construction of the furnace as proposed by Steger in the above-named treatise is shown in Figs. 227 and 228, the first a longitudinal and the second a transverse section of the furnace; *a* are three retorts built of magnesia bricks with arched roof and floor. Between the separate retorts there are flues *d*, in which the producer gases are burnt by means of heated air, these gases being led by means of slots

<sup>1</sup> Ger. Pat. 91896.

<sup>2</sup> *Zeitschr. für das Berg-, Hütten- und Salinenwesen*, 1900, p. 411.

<sup>3</sup> *Preuss. Minn. Ztschr.*, 1894, p. 163.

from the shafts *c*, into the flues *d*. The air for combustion is heated in the retort *W*, and then enters the flues *d*. The products of combustion escape through slots into the vertical flue *e*, pass at the upper end thereof into the flue *f*, and finally through *g* to the stack. Hereby the bottom as well as the top of the muffles are completely surrounded by the flame. The retorts are charged and emptied at their back ends where they open out into a vertical flue, *p*. The gases and vapours which escape during the charging and drawing rise up in this flue, whilst the distillation residues fall downwards. The adapters, *i*, are at the front ends of the retorts in a vertical chamber, *h*, to the back-wall of which the retorts are secured air-tight. There are no statements regarding the dimensions of the retorts. Their size and thickness are to be calculated from the conductivity of the magnesia, from the heating

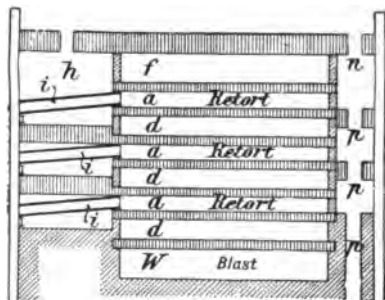


FIG. 227.

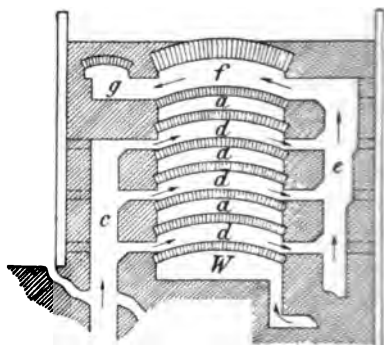


FIG. 228.

capacity of the gas flues, and from the conductivity of the material of the charge. The advantages of the magnesia vessels which are chiefly dwelt upon by Steger, are their great durability, the small loss of zinc during the operation, the possibility of charging them with ore in the finest state of division, the non-existence of any necessity for replacing retorts, greater durability of the adapters and larger dimensions of the latter, more rapid charging and drawing, and easier and more healthy work. Steger's furnace has been patented in the name of the owner of the works, Francisci, in Schweidnitz.<sup>1</sup> Experiments with this furnace are now being tried in Silesia. The magnesia bricks at first used showed themselves to be very sensitive to changes of temperature. It is still hoped, however, that a suitable material will be found. A recent furnace of Francisci with vertical circular retort, which may be made of magnesia bricks, and heated

<sup>1</sup> D. R.-P. 76285; Belgian Pat. 107606; British Pat. No. 23979; Austrian Pat. 44/3256; American Pat. 526808.



from the inside and outside of the retort, has been pictured and described on p. 128. Any definite opinion upon these retorts can only be given when the results of long working are known. These results are not yet forthcoming.

Landsberg has proposed to make retorts with an inside coating of graphite and fire-clay, and an outside coating of fire-clay, the idea being that the inside will not be attacked by the charge, and the outside clay will protect the graphite inside from the action of the fire. Hering<sup>1</sup> has proposed muffles for continuous working. These are represented in Figs.

229 and 230. The muffle *a*, open below, stands over the tunnel *b* which receives the distillation residues. The muffle is closed by the residues from the foregoing distillation. The residues can be removed from the tunnel through the opening *C*, which can be closed when need be. The muffles are charged through the hoppers *g* and the

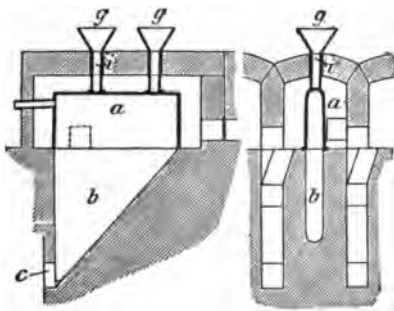


FIG. 229.

FIG. 230.

clay pipe *i*. After charging, the hopper is closed by a clay plug. It is doubtful whether these muffles will prevent the access of air to the charge. They have not yet found practical application. Sadtler<sup>2</sup> has proposed to use retorts of clay coated inside, and on specially exposed places outside, with burnt dolomite or magnesite. These are to be used for the extraction of zinc from ores containing gold, silver, lead and iron. The coating is affixed by means of water glass, which fuses together the clay and the basic covering. This is brought about by heating the retorts in the furnace at a temperature of 816° C. for several days after they have been coated with the water glass and the basic material. This basic lining is said to withstand the action of the oxides of lead and iron. Gold and silver remain with the distillation residues and can be recovered from them. There is no information about the application and durability of these retorts.

*Proposals for the Extraction of Zinc from Blende, without previous Sweet-Roasting of the same.*

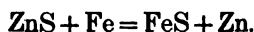
None of these proposals have yet been practically developed. Biewend's suggestion<sup>3</sup> to decompose zinc blende by heating it in a

<sup>1</sup> *Zeitschr. für das Berg- Hütten- und Salinenwesen*, 1900, p. 420.

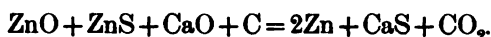
<sup>2</sup> U.S. Pat. 656268.

<sup>3</sup> Ger. Pat. 81358, August 7, 1894.

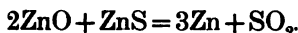
shaft furnace with iron, has already been described. Grillo and Liebig<sup>1</sup> suggest decomposing zinc blende with molten iron in a tightly closed cylindrical apparatus which can be rotated. In this way sulphide of iron and zinc would be formed, and the zinc being liquid at the pressure obtaining in the cylinder, would collect below the iron sulphide and could be tapped after cooling down. The reaction taking place may be expressed by the equation:—



Landsberg proposes to heat a mixture of raw and roasted zinc blende with lime and coal in the absence of air; the zinc vapour thus formed would then be condensed. The reaction takes place as follows:—



Christopher James suggests heating the mixture of raw and roasted blende in the indifferent or feebly reducing atmosphere of a reverberatory furnace, the decomposition taking place according to the equation:—



This method, however, does not seem feasible, for the required atmosphere cannot be produced in a reverberatory furnace, nor does the reaction take place as represented by the equation.

#### *Proposals to obtain Carborundum and Ferro-Silicon along with Zinc*

According to Dorsemagen,<sup>2</sup> when zinc ores rich in silica (roasted zinc blende) are heated with enough coal to reduce not only the zinc oxide but also the silica, there is formed, besides zinc, carborundum or silicon carbide. The construction of the furnace for this process is not given, but is said to be quite simple. Blende containing pyrites can be made to yield zinc and ferro-silicon, according to the same authority, when after preliminary roasting it is mixed with quartz materials and reduced with coal in the electric furnace. No information is to hand concerning the application of these proposals.

#### *The Production of Zinc by Electro-thermal Methods*

Though many methods for obtaining zinc electro-thermally have been proposed, none of them have found definite application. In 1885 the brothers Cowles<sup>3</sup> suggested heating charges by electric

<sup>1</sup> Ger. Pat. 92243.

<sup>2</sup> *Zeits. d. Ver. d. Ingenieure*, 1902, p. 1635

<sup>3</sup> Ger. Pat. 34730

current in tubular retorts of fireclay, which are surrounded by bad conductors of heat. One of the terminals was to be connected with a slab of carbon which served to close one end of the retort, while the other terminal was connected with a graphite crucible which closed the other end of the retort and served as a receptacle for the zinc. It was proposed to mix the ore intimately with some substance of high resistance, preferably with carbon used in electric lighting, then to charge the mixtures into the retorts, and to reduce the zinc at the high temperature produced on completing the circuit. The zinc vapours were to be led off through a hole in the graphite crucible and condensed, and the carbon monoxide to escape through a pipe in the fore end of the crucible. This method has not come into use; nor has that of Siemens and Halske,<sup>1</sup> in which circular terminals were used. Experiments carried out in this way only led to the production of zinc dust. The method of Casaretti and Bertani<sup>2</sup> does not seem to have found practical application.

M. A. Salguès<sup>3</sup> in his attempts to prepare zinc in the electric furnace at Crampagna, Ariège, obtained only zinc fume; with zinc ores, however, he succeeded in obtaining zinc white, and his method is in definite use at Crampagna for that purpose.

Edelmann and Wallin have proposed the heating of the charge in the arc of the electric furnace, air being excluded by the charge itself. The zinc vapours are led away at the temperature suitable for the condensation of liquid zinc, and the gangue is slagged off, and along with the reduced lead flows into a holder where the two can be separated. The furnace has an upper bell-shaped electrode, and a lower ring-shaped electrode, and the process is continuous. No further information is forthcoming about this well-conceived process, nor has it yet been definitely applied. Dorsemagen's<sup>4</sup> proposal described above to prepare carborundum along with zinc, has given good results on an experimental scale. The furnace used in the trials had closed crucibles with carbon electrodes, and a side adapter to receive the zinc. For description see Borchers' *Elektrometallurgie*, p. 386. This same furnace<sup>5</sup> has been used successfully

<sup>1</sup> Ger. Pat. 100921.

<sup>2</sup> *The Min. Ind.*, 1902, p. 266; 1903, p. 235. For description of the furnace and the methods of working see *Electrochem. Zeit.*, December, 1902.

<sup>3</sup> *Mémoires et Compte rendu des Travaux de la Société des Ingénieurs Civil de France*. Juillet, 1903, p. 64.

<sup>4</sup> Ger Pat. 128535.

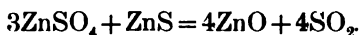
<sup>5</sup> *Denkschrift der K. t. Hochschulen zu Aachen aus Anlass der Industrie Gewerbe- und Kunstausstellung zu Düsseldorf im Jahre, 1902*, p. 48, also Borchers, *Das neue Institut für Metallhüttenwesen und Electrometallurgie an der K. t Hochschule zu Aachen*, Halle, 1903, p. 13.

to obtain zinc and ferro-silicon from calcined zinciferous pyrites. If the ores are lacking in silica and bodies containing iron, these are added in such quantity that a 25 per cent. ferro-silicon is produced.

### THE EXTRACTION OF ZINC BY THE COMBINED WET AND DRY METHODS

The direct extraction of zinc by the wet method is not possible because zinc cannot be thrown down in the metallic form from its solution by any metals that are permanent at ordinary temperatures. Apart from the separation of this metal by electrolysis, only compounds of zinc can be produced in the wet way, from which the zinc must be reduced in the dry way. The wet method of zinc extraction can therefore only be looked upon as an auxiliary process for the dry method, in which the zinc is obtained from ores and metallurgical products in the form of aqueous solutions, from which compounds of zinc can be obtained that can be converted into oxide. The reduction of the oxide to metallic zinc is performed in the dry way. The combined wet and dry way of zinc extraction has, however, up to the present been found to be too dear for practical purposes. Zinc has been extracted from poor ores and furnace products by means of sulphuric acid, hydrochloric acid, ammonia, ammonium carbonate, magnesium chloride, calcium chloride, carnallite, and by a chloridising roasting followed by leaching of the chloride of zinc so formed, the products being solutions of zinc sulphate, zinc chloride, ammonio-zincic hydrate, and ammonio-zincic carbonate respectively. Zinc oxide has been produced from the solution of the sulphate by evaporating the latter and heating the zinc sulphate obtained, sulphuric anhydride and sulphurous oxide and oxygen being given off. The zinc oxide can be efficiently treated for zinc in muffles, but so far, zinc oxide has not been prepared on a large scale by this method owing to the costliness of the process.

Parnell proposes<sup>1</sup> to obtain zinc sulphate by treating calcined ores containing zinc oxide with sulphuric acid, to evaporate the sulphate solution until it commences to thicken, then to stir sulphide of zinc into the mass, and to heat the mixture in a muffle furnace. Sulphur dioxide, which is to be used for the manufacture of sulphuric acid, is said to escape while zinc oxide is formed, in accordance with the equation:—



This reaction is probably very imperfect, as it is not possible to

<sup>1</sup> *Kärnthner Ztschr.*, 1881, p. 32.

convert the whole of the zinc into zinc oxide. This proposal has not, therefore, found any employment.

W. Marsh has proposed to precipitate zinc hydrate from a solution of the sulphate by means of magnesia. On account of the high cost of magnesia, this process cannot be employed upon a large scale. By heating anhydrous zinc sulphate with carbon, zinc oxide along with carbon monoxide and sulphur dioxide is formed when the mixture is intimate and the right temperature is preserved. This method has proved too expensive.

Hoepfner<sup>1</sup> has proposed the precipitation of zinc sulphide from zinciferous liquors by hydrogen sulphide, and the heating of the sulphide with lime and coal to obtain zinc and calcium sulphide. The calcium sulphide might then be used for the preparation of hydrogen, sulphide, and the filtrate from the former for the solution of zinc from bodies containing it in the form of oxide. The suggestion has not yet found application.

Zinc chloride can be obtained by the treatment of bodies containing the oxide or carbonate of zinc with hydrochloric acid, magnesium or calcium chloride, or with carnallite, or by the calcination of zinc blende with common salt; and zinc oxide can be obtained cheaply by treating the solutions so produced with milk of lime. In addition to zinc oxide or hydrate, zinc oxychloride is also formed, and this method for the production of zinc oxide has been found to be unsuitable for operations on a large scale.

Of the salts of ammonia, carbonates show the greatest capacity for dissolving zinc oxides from ores and products,<sup>2</sup> having considerably greater dissolving powers than has ammoniacal liquor. The most suitable solutions are those containing 7 to 8 per cent. of ammonia and 7 to 8 per cent. of carbon dioxide. By distilling off the ammonia and the greater part of the carbon dioxide, the zinc can be separated as a basic carbonate, whilst the solution is regenerated, with the exception of a certain quantity of carbon dioxide which has to be replaced. The basic zinc carbonate can be converted into oxide by heating. This method is too expensive for the extraction of zinc from poor ores, and has therefore only been used for the extraction of zinc oxide from argentiferous metallurgical products.

Although, therefore, the combined wet and dry method of zinc extraction from poor ores has not yet passed the experimental stage for the reasons above stated, it has nevertheless come into use in those cases in which the object is not the extraction of metallic zinc, but the separation of zinc from other valuable metals and metallic

<sup>1</sup> *Kärntner Zeits.*, 1881. p. 32.

<sup>2</sup> Schnabel, *Preuss. Ztschr.*, vol. xxviii.

compounds, and the conversion of the zinc into a bye-product in the form of merchantable compounds such as zinc vitriol, zinc chloride, basic zinc carbonate or zinc white, as also for the production of zinc salts from residual products containing zinc. Whether and to what extent the wet method may in the future find employment as an auxiliary process to the dry way for the production of compounds rich in zinc from ores or artificial products poor in zinc cannot at the present day be decided. Stahl<sup>1</sup> has determined by a series of experiments to what extent the zinc contained in burnt pyrites can be converted into chloride by chloridising roasting, and what proportion of zinc volatilises in this process. The zinc is contained in the burnt ore as sulphide, sulphate and oxide. It was not found possible to convert the zinc in pyritic residues containing 7 to 11 per cent. of zinc completely into chloride by a single chloridising roasting even although pyrites was added, which greatly promoted the formation of sulphate. On the other hand, the chloridising of zinc was almost complete when the once roasted and then leached ores were submitted to a second chloridising roasting with the addition of pyrites. Only 2 to 3.5 per cent. of zinc volatilised during calcination in the form of zinc chloride, which was caught again in condensing towers.

Stahl<sup>2</sup> proposes to work the liquors got by leaching the roasted mass, for zinc white, zinc sulphide, lithopone and *blanc fixe*, after these liquors, which contain chiefly chloride of zinc and sodium and sodium sulphate, have been deprived of any heavy metals they might contain by precipitation. The proposed method is to precipitate the gold, silver, copper, lead and cadmium by addition of zinc scrap to the warmed solution, the spongy metallic mass being then treated for these various metals by the ordinary methods. The liquors from this precipitate, which contain lead, copper, cadmium, arsenic, antimony, nickel and cobalt, are then treated with sodium sulphide, which precipitates these metals as sulphides mixed with some zinc sulphide. The filtrate from the sulphide precipitate is now worked for the metals which are present in quantity, and finally for cadmium. The zinc is converted into zinc chloride, and this is treated for lithopone. To remove iron and manganese, a little bleaching powder is added to the warmed liquor to oxidise the ferrous to ferric salts, then soda is added, until the liquor is alkaline, and after this more bleaching powder to the warmed liquid. This precipitates iron, manganese, and part of the zinc, and the filtrate from these is suitable for the preparation of zinc white, zinc sulphide, lithopone (a mixture of barium sulphide and zinc sulphide) and *blanc fixe*.

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1894, p. 1.

<sup>2</sup> *Ibid.* 1898, p. 1.

(barium sulphate). The precipitate obtained with bleaching powder is washed with soda solution to remove chlorine in the form of sodium chloride, and is sold to the zinc smelting works. This process has not become established on a working scale.

A proposal emanating from the Maria Works at Langelsheim<sup>1</sup> is to produce zinc chloride and barium chloride from the slags containing these metals, which are obtained in smelting zinciferous lead ores at the Lower Harz Works. The proposed method is to convert the barytes into barium chloride and calcium sulphate by an ordinary roasting of the powdered slags with calcium chloride at a temperature of 1,200° C. in a reverberatory furnace. After the barium chloride has been leached out of the melt, the residue consisting of calcium sulphate and the sub-silicates of lead and iron, is to be treated in a lead pan with sulphuric acid (50° B), then to be mixed with calcium chloride and the zinc converted into chloride by heating this mixture in a muffle furnace to 500° C., stirring frequently the while. The iron also is first converted into chloride during this reaction, but is decomposed at that temperature into ferric oxide and hydrochloric acid, and the acid may be collected and used to regenerate calcium chloride. The zinc chloride is then to be leached out of the heated mass, and the residue of calcium sulphate and ferric oxide, after drying and grinding, might be used as a red dye. It is probable that this method could be worked with advantage, if the technical difficulties be not too great.

### THE ELECTROLYTIC EXTRACTION OF ZINC

The electrolytic extraction of zinc is quite modern. Up to the present the extraction of zinc in the wet way only has been the object of continuous energetic experiments, and, in fact, in some cases the process has been actually employed upon a working scale. The extraction of zinc in the dry way by the electrolysis of molten compounds of the metal has not yet been attempted on a working scale, although propositions in this direction are not wanting. We have first to consider the electrolytic extraction of zinc in the wet way, and then the proposals for its electrolytic extraction in the dry way.

#### *The Electrolytic Extraction of Zinc in the Wet Way*

As far as is known, experiments with this object were first made at the end of the seventies by Luckow in Deutz, and at the com-

<sup>1</sup> Ger. Pat. 112018,

mencement of the eighties by Letrange, of Paris, without their experiments leading to any satisfactory results. Not only are the technical difficulties great in the electrolytic extraction of zinc, but the costs of working are high. The main difficulty is to prevent the separation of the zinc in a spongy form. The chloride and sulphate of zinc, the two most important salts of zinc from the electro-metallurgist's point of view, both give spongy zinc very readily when their solutions are electrolysed. The spongy zinc cannot be melted down as it burns in greater part at the temperature necessary to melt it. This happens also when compressed zinc sponge is melted, or when it is added to a bath of zinc. With suitable current densities, the formation of zinc sponge during electrolysis depends on the absorption of oxygen and the oxidation of a relatively small quantity of zinc, whereby oxide or a basic salt of zinc is precipitated along with the metal. This happens when there are metals present in solution which have a smaller solution tension than the zinc; when the solutions are very weak, *i.e.* when the concentration of zinc ions is small, and that of hydroxyl-ions is great; when certain oxidising agents like hydrogen peroxide and nitrates are present; when the precipitate is very uneven (in which case it encloses some of the electrolyte, which becomes neutral and deprived of zinc ions); and when hydrogen bubbles cling to the cathode, with the result that the zinc is deposited unevenly between the bubbles, and enclosing liquor prevents its renewal. The formation of spongy zinc is obviated by keeping the electrolytes free from foreign metals, by preserving the concentration and slight acidity, by circulation of the liquor and by removal of gas bubbles from the cathode.

The high costs of electrolysis are due to the absorption of much electrical energy, to the expensive methods of preparing the electrolyte, to the care needed to avoid uneven precipitation of the zinc, and to the corresponding high cost of plant. With regard to the first item, the bath tension, when insoluble anodes are used, must be at least 2.5 volts, since the decomposition tension of zinc sulphide is 2.35 volts, and of zinc chloride 2.43 volts. In consequence of these drawbacks, the electrolytic preparation of zinc has only come into extended use in few places. It has been tried at many works, and given up on account of unfavourable technical and economic results. It is at present in use at Winnington, in England, for the preparation of zinc from zinc chloride solution, and at Friedrichshütte, in Tarnowitz, for the treatment of zinc-silver alloys.

Owing to the great interest which this subject arouses, the most important experiments which have been made to clear up the



question of the formation of spongy zinc, and the proposals which hinder this formation, will be now passed in review.

Kiliani found, in the course of his experiments<sup>1</sup> to determine the conditions of the deposition of compact zinc from solutions of zinc vitriol, that, even when soluble anodes were employed, if the current tension was low, gas was evolved, and the zinc became spongy; but that, on the other hand, if the current tension was high and the solutions not too dilute, no gas was evolved, and the zinc was compact and brilliant. He also found that when highly dilute solutions were employed, hydrogen was actively evolved, and that the zinc was always spongy, whether the current was feeble or strong. With feeble currents, zinc oxide, together with zinc, was deposited from dilute solutions. For instance, from a solution containing 1 per cent., with a current tension of even 17 volts, oxide of zinc was deposited when only 0.0755 gram of zinc was thrown down per minute upon a 1 square centimetre of cathode area. The results of Kiliani's experiments are shown in the following table.<sup>2</sup> They refer to a solution of zinc vitriol of specific gravity 1.38, anodes and cathodes being made of sheet zinc:—

Zinc deposited per minute per sq. centimetre of cathode surface.	Ampères per square metre.	Gas evolved per 1.5 grams of zinc deposited.	Nature of the deposit.
Milligrams.		Cub. cent.	
0.0145	7	2.40	Very spongy.
0.0361	18	2.27	"
0.0755	38	0.56	"
0.3196	158	0.43	More compact, but spongy at the edges.
0.6392	316	0.33	Can still be wiped off readily.
3.7274	1,843	—	Firm and lustrous, with bud-like projections round the edges.
38.7750	19,181	—	

From a 10 per cent. solution, Kiliani obtained the best deposits when the current was equal to 0.4 to 0.2 milligramme of zinc. Hence it seems that excessively great current density is necessary to produce a compact deposit of zinc. As, however, the zinc deposited from strong solutions by the application of relatively low current densities, is not always spongy, Kiliani's experiments require confirmation. It is possible that other, still unknown, causes were at work under his experimental conditions.

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1883, p. 251.

<sup>2</sup> Borchers, *Elektro-Metallurgie*. Brunswick, 1891, p. 96.

Nahnsen,<sup>1</sup> in his experiments to determine the most suitable current densities and temperatures for the deposition of compact zinc from solutions of zinc vitriol, found that hydrogen (primarily generated by the addition of sulphuric acid to the solution of zinc vitriol, plates of zinc being used as anodes), which formed in great quantity at the cathodes, does not make the zinc spongy, and therefore assumed that the sponginess was due entirely to the formation of zinc oxide. According to him, the hydrogen which appears at the cathode simultaneously with the spongy deposits, is of a secondary nature, produced by the action of the deposited zinc upon the water of the solution. Nahnsen further tried experiments upon the character of the zinc deposited at various tensions and temperatures. These were tried upon solutions of zinc sulphate whose specific gravities at 18° C. were respectively 1·0592, 1·1233, 1·1925, 1·2710, 1·3543, and 1·4460, using soluble anodes in the form of zinc plates of 0·054 square foot in area. The results obtained are shown in the following table, in which the density of the current, the temperature of the electrolyte, and the character of the deposit are indicated:—

Current density. Amperes per sq. foot.	Temperature of the electrolyte.			
	+ 0·97° C.	+ 10·68° C.	+ 20·72° C.	+ 30·47° C.
0·93	Compact	Spongy	Spongy	—
4·57	„	Spongy at first	„	—
9·13	„	Compact	Spongy at first	Spongy.
13·60	—	„	Compact	Spongy at first
18·20	—	„	„	Compact

According to Nahnsen other salts of zinc showed similar relations between temperature and current density, but the limits of current strength and temperature are different from those obtaining in the case of sulphates. For instance, a solution of zinc nitrate, moderately concentrated, evolved hydrogen even at 0° C. with a current density of 9·4 amperes per square foot; whilst such evolution no longer occurred at -12° C. Whilst Kiliani, using a solution of zinc sulphate of 1·38 specific gravity, with a current tension of 30 amperes per square foot, obtained a deposit of zinc which could be readily wiped off, Nahnsen at a temperature of + 30° C. obtained from a solution of zinc sulphate of approximately equal concentration with a current density of 18·8 amperes per square foot a perfectly solid deposit of

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1893, p. 393.

zinc. When large electrodes, 3 feet 3 inches by 1 foot 8 inches, were used, the latter obtained at a temperature of  $+21^{\circ}\text{C}$ . an unexceptionable deposit of zinc with a current density of 7 ampères per square foot. When he employed electrodes of 5.4 to 10.8 square feet in area, he obtained good zinc with a far less current density than could have been expected from the experiments carried out with the above electrodes of 0.05 square foot in area. The high current tensions found by Kiliani are explained by him by the circumstance that the latter worked with small electrodes; and he ascribes the fact that the influence of current density and of temperature upon the nature of the zinc deposit decreases with the increase of the area of the electrodes, to the action of the edges of the latter. The current density is greater at the edges of the electrodes than in the centre part, and therefore diminishes the average total density, this diminution being the more noticeable the smaller the electrodes are. Nahnsen's view<sup>1</sup> that the baths must be cold in order to get a compact zinc deposit, has been proved to be erroneous by Siemens and Halske, who repeated Nahnsen's experiments without being able to confirm them. In fact, the contrary was found to hold, warming the electrolyte being advantageous. Coehn<sup>2</sup> is of the opinion that the formation of spongy zinc is due to the evolution of hydrogen, and states that the formation of this body can be prevented at the cathodes even with low current density by interrupting the current from time to time. Thus he claims to have produced a compact deposit with a current density as low as 4.7 ampères per square foot in the electrolysis of zinc sulphate by interrupting the current 50 times per minute. During the interruption the current was made to traverse a second bath, these interruptions being produced by special mechanical contrivances. Cowper-Coles<sup>3</sup> attempts to produce dense deposits of zinc by increasing the current density from time to time in intervals of about 8 minutes. Hoepfner<sup>4</sup> considers that an active motion of the electrolyte by means of rotating cathodes is necessary for the production of dense deposits. In this way hydrogen bubbles, which have clung to the cathodes, are removed, and the formation of ragged edges by abnormally high and uneven current densities is prevented. Mylius and Fromm<sup>5</sup> agree with Nahnsen in ascribing the cause of the formation of spongy zinc to the formation of zinc oxide or of basic salts. They regard spongy zinc as zinc which has

<sup>1</sup> Dinger's *Polytech. Journ.*, vol. cclxxi. 4, p. 81.

<sup>2</sup> D. R.-P. No. 75482, 1893.

<sup>3</sup> D. R.-P. No. 79447, 1894.

<sup>4</sup> English Pat. No. 13336, 1893.

<sup>5</sup> *Zeitschr. f. Anor. Chemic*, vol. xix., 1895.

been disturbed in its crystallisation by the absorption of oxygen. If the conditions are not favourable to the formation of zinc oxide, no sponge is produced. On dissolving zinc sponge in mercury they always obtained a residue containing zinc oxide or a basic salt, the amount of which was less than 1 per cent. of the weight of the sponge. If oxidising agents were present during the electrolysis of a solution of zinc sulphate, zinc sponge was always formed, whilst in the absence of such bodies deposits of smooth white zinc were obtained. For example, a 10 per cent. neutral solution of zinc sulphate, with a current of 10 ampères per square foot, formed sponge at the end of two minutes in the presence of 0.01 per cent. of hydrogen peroxide. When the electrolyte contained 0.1 per cent. of zinc nitrate as an oxidising agent, a blackish-gray deposit of zinc containing oxide formed at the end of one minute. This deposit contained zinc nitrate and requires further investigation. A cathode of sheet zinc which had been touched in several places with turpentine containing oxygen, showed at once the commencement of the formation of zinc sponge by the development of grayish-black stains at the spots that had been touched. From a 10 per cent. solution of sulphate of zinc into which zinc oxide had been stirred, with a current density of 10 ampères per square foot, five minutes after the commencement of the electrolysis gray spongy zinc was deposited upon the cathode of sheet zinc in a streak along the surface of the solution. The presence of foreign metals in the electrolyte promotes the oxidation of zinc (galvanically), and therefore the formation of sponge. Thus a 10 per cent. solution of zinc sulphate which contained 0.004 per cent. of arsenic in the form of ammonium arsenite, gave evidence of the formation of spongy zinc after electrolysis for only one minute. According to the views of Mylius and Fromm, sponge cannot be deposited from acid solutions of sulphate of zinc.

Neutral concentrated solutions of zinc sulphate dissolve small quantities of zinc oxide, so that these solutions give compact zinc during the first hour of electrolysis. The liquid, however, soon becomes basic, due to the oxidation of zinc, and the sponge is then deposited. To prevent this, it is necessary to maintain the solution slightly acid; continuous agitation of the liquid is further necessary, otherwise it becomes dilute at the cathode, owing to the different velocities of the two ions, and sponge always separates out from weak basic solution. According to Mylius and Fromm, sponge can be produced owing to want of uniformity in the quality of the electrodes. This happens, for instance, when capillary spaces, en-

closing electrolyte, are formed between the outstanding zinc crystals in the cathode. This enclosed liquid becomes neutral and impoverished in zinc ions, and the formation of sponge is thus set up. As soon as sponge is developed at any one spot, the liquid passing through it is quickly deprived of its zinc, owing to the uneven current densities in the neighbourhood and the restricted movement of the electrolyte, and as a consequence abundant liberation of hydrogen takes place, and opportunity is afforded for the formation of a further quantity of sponge. Bubbles of hydrogen formed on the cathode even in weak acid solutions can occasion the precipitation of sponge, by causing uneven precipitation of the zinc and hindering thereby the renewal of solution at many places at the cathode surface. Thus Förster and Günther<sup>1</sup> observed that a strongly acidified and but little agitated solution of zinc sulphate gave on electrolysis first a honeycomb mass of zinc, built round large bubbles of hydrogen which clung tenaciously to the cathode, and afterwards a considerable deposit of sponge. Hence Mylius and Fromm state that too much free acid in the electrolyte should be avoided, otherwise hydrogen is liberated at the cathode along with zinc, and the gas bubbles cling for some time to the surface.

Results similar to those of Mylius and Fromm have been obtained by Förster and Günther, working with neutral acid and basic solutions of zinc chloride (instead of sulphate) and soluble anodes made of electrolytic zinc from Upper Silesia. The anode zinc contained 0.03 per cent. of lead and 0.05 per cent. of iron, the electrolyte was freed from cadmium before use, and was kept in agitation by a stirrer. The results were as follows:—

*Neutral* solutions of zinc chloride containing 54.6 grams of zinc per litre were electrolysed with a current density of 116 ampères per square yard. The zinc first formed was compact; after 20 hours it had become spongy and the electrolyte was turbid, due to the separation of basic zinc chloride. This was filtered off and the filtrate again electrolysed, when the deposited zinc became spongy even after a few hours.

It was sought to prevent the formation of sponge by addition of chlorine to the electrolyte, but the result was unfavourable, as the sponge was formed even after a few hours; slightly acid solutions were also tried without success. Atmospheric oxygen in presence of zinc chloride oxidised zinc rapidly; so that in these experiments basic zinc chloride was formed, the solution lost its power of dissolving zinc oxide, and sponge was formed in consequence. The deposition of

<sup>1</sup> *Zeit. für Electrochem.*, No. 1. July 7, 1898, p. 16.

sponge was obviated as long as the solution retained its power of dissolving zinc oxide, and remained clear thereby.

*Acid* solutions of zinc chloride gave a deposit of compact zinc. It was found requisite to add acid from time to time to replace the acid neutralised by the zinc oxide formed in the process. The best results were obtained with solutions of  $\frac{1}{20}$  to  $\frac{1}{30}$  normal strength of hydrochloric acid. If the strength of free acid was over  $\frac{1}{10}$  normal, then considerable evolution of gas took place at the cathode and the zinc had a warty appearance. This drawback, which was also noticeable to some extent when the solutions were much less acid, could be corrected by keeping a little chlorine in solution. The action of the chlorine was to prevent the hydrogen bubbles from lingering too long at one place, occasioning thereby unevenness in current density and concentration at the surface of the cathode. In this way zinc free from arsenic was successfully prepared from commercial zinc. The cathodes had a total area of  $\frac{1}{2}$  square foot, the current strength was 5.5 ampères, equal to a current density of 167 ampères per square yard, and the tension 0.9 volt. To remove hydrogen bubbles from the cathode, air can be blown through the electrolyte, which promotes in addition the circulation of the liquid. It was found, however, that owing to the rapid oxidation of the zinc at the electrodes, the free acid was neutralised much more quickly than when chlorine was used, so that the latter is to be preferred.

The *basic* solutions of zinc chloride contained 150 grams of zinc and 157.7 grams of chlorine (*i.e.* 4.82 grams of zinc as zinc oxide) in a litre of the solution. The electrolyte was heated to 60° C. and a current density of 125 ampères per square yard was employed. At first the deposited zinc was compact; after a short while, however, a fine branching growth began at the edges and spread over the whole of the cathode. As the electrolyte grew more and more alkaline and became turbid, the experiment was stopped.

The experiments of Förster and Günther point to the conclusion that sponge is formed from solutions of zinc chloride only when they contain a large amount of suspended oxychloride which they are no longer able to dissolve. Upon the results of these experiments Förster and Günther base their opinion that sponge is formed in neutral or slightly basic solutions of zinc chloride and sulphate, when these solutions become so impoverished in zinc and hydrogen ions that the concentration of the residual hydroxyl ions at the cathode exceeds that of solutions of zinc hydroxide or basic sulphate and chloride of zinc. If these compounds separate out along with the zinc at the cathode, then the process of crystallisation and the

deposition of a uniform coating is disturbed, and the opportunity arises for the formation of spongy masses. Hydrogen is always evolved from weak solutions of zinc salts, and in the precipitation of metals which are more electronegative than zinc. These metals increase the formation of zinc oxide, the further they are removed from zinc in the order of tension. It is, therefore, necessary to remove them from the electrolyte before beginning the electrolysis.

According to Förster and Günther, the formation of sponge can be hindered by keeping the electrolyte slightly acid, as this prevents any considerable concentration of hydroxyl ions. If soluble anodes be used the acid must be renewed continuously, as it becomes exhausted by the liberation of hydrogen and by its neutralisation with the zinc oxide formed by oxidation of the zinc by atmospheric oxygen. It is also needful to keep the acid electrolyte in fairly rapid motion at the cathode, otherwise those portions of the liquid in the immediate neighbourhood of the plate may become neutral or basic, and thus give rise to the formation of sponge. Further experiments on the influence of oxidising agents on the formation of sponge show that the action is promoted in neutral solutions by ammonium nitrate and hydrogen peroxide, while in acid solutions, though the former substance retains its power (in  $\frac{1}{10}$  normal sulphuric acid), the latter loses it. The halogens and ammonium persulphate hinder the formation of sponge.

Compact zinc was formed in presence of potassium permanganate to the extent of 0.1 gram in a neutral solution of 250 grams of zinc sulphate in 1 litre of water, the current density being 84 to 125 ampères per square yard. Manganese peroxide is thrown down along with this, and as this body can combine with zinc oxide, it is possible, according to Förster and Günther, that the cause of the disturbed crystallisation of the electrolytic zinc lies in this reaction.

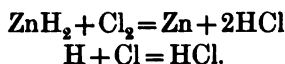
According to Siemens and Halske, the formation of spongy zinc is due to the presence of small quantities of hydrogen and traces of zinc hydride ( $\text{ZnH}_2$ ). To avoid this objection,<sup>1</sup> they propose to fix the hydrogen by means of free halogens, or by such halogen compounds as will combine with the hydrogen with the formation of the respective hydrides. Among such bodies applicable to a solution of sulphate of zinc may be named a weak solution of chlorine, bromine or iodine, or a weak solution of free hypochlorous or hypobromous acid, or chlorine or bromine gas, or chlorine and bromine substitution products of organic bodies which are soluble in water, and which give up their chlorine or bromine, and are thus reduced to lower compounds by

<sup>1</sup> D. R.-P. No. 66592.

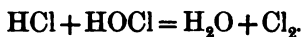
nascent hydrogen, as, for instance, the soluble chlorhydrine of glycerol and other glycols. When an excess of chlorine is present in the solution of zinc sulphate, hypochlorous acid is always formed according to the following equation :—



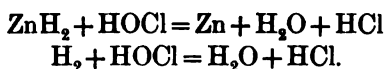
The chemical changes that take place when the above bodies are added are the following :—Free chlorine forms hydrochloric acid with either hydrogen or with the hydrogen of zinc hydride, as is shown in the following equations :—



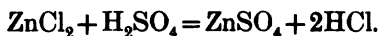
As these substances are only employed in very small quantities, the hydrochloric acid produced is too dilute to have any dissolving action upon the cathode. The dilute hydrochloric acid, however, forms free chlorine with hypochlorous acid formed as above, as shown in the following equations :—



Hypochlorous acid or hypobromous acid acts as follows upon zinc hydride and hydrogen :—



The zinc chloride formed by the action of chlorine upon zinc is transformed into zinc sulphate by the sulphuric acid liberated at the anode and diffusing from it through the solution, as shown by the following equation :—



The hydrochloric acid thus formed again forms free chlorine with the hypochlorous acid.

The chlorine liberated in these various reactions continually acts over again in the above manner. In the presence of hypochlorous acid in the solution the chlorine is accordingly regenerated to a very large extent. Zinc deposited with the addition of these bodies is said to be compact and of a silvery colour. It is necessary, in conducting the process, that the fluid to be electrolysed shall constantly show a distinct reaction of the free halogen or of the active oxycompound of that halogen.



Mylius and Fromm<sup>1</sup> consider that the above opinion of Siemens and Halske, that the formation of zinc sponge can be prevented by the destruction of zinc hydride as above, is not tenable. They refer the action of chlorine, iodine, hypochlorous acid, &c., merely to the fact that these bodies are acid formers. According to Borchers,<sup>2</sup> it has not been proved that zinc hydride is formed when zinc salts are electrolysed. He is of the same opinion as Mylius and Fromm, and adds that in the presence of sulphurous acids, phosphorous and hypophosphorous acids, *i.e.*, of reducing agents, he has obtained the same results as were produced by Siemens and Halske by means of chlorine, bromine, iodine, &c. According to the experiments of Nahnsen, zinc is thrown down in the spongy form when the solutions of zinc salts are rendered impure to any great extent by the presence of other metals. In addition to the absolute quantity of these foreign bodies present, the strength of the zinc solution and the density of the electric current are also important. With 1 lb. of zinc to 1 gallon of solution, 0·004 oz. of copper in the gallon have, according to Nahnsen, no effect upon the character of the deposit. With  $\frac{1}{2}$  lb. in one gallon there is a distinctly perceptible evolution of gas. With 0·016 oz. to the gallon there is evolution of gas and the deposit at the same time becomes slightly warty. With 0·024 oz. this wartiness appears earlier and more strongly marked; and with 0·048 oz. in the gallon the zinc is thrown down in the spongy form.

With 3·2 oz. of zinc in the gallon of solution as little as 0·0016 oz. of copper in the gallon produces a few scattered spots. With 0·008 oz., the whole electrode becomes warty, and with 0·02 oz. of copper in the gallon the deposit becomes spongy at the end of 55 minutes. Cadmium, silver, arsenic, and antimony are said to behave like copper; iron is said to promote the evolution of hydrogen and to render the baths impure by the separation of ferric and ferrous oxides, without having, however, any influence upon the formation of spongy zinc, as long as the quantity is not excessive. For instance, according to Nahnsen, with 3·2 oz. of zinc and 0·32 oz. of iron as protoxide in the gallon of solution, no sponginess was noticeable; neither was there any with the same amount of zinc and 0·4 oz. of iron in the form of peroxide.

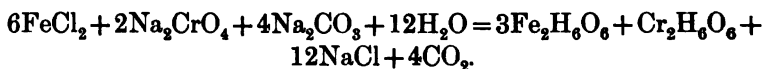
Mylius and Fromm<sup>3</sup> assume that those foreign metals which promote the oxidation of zinc electrically give rise to the formation of sponge. According to their experiments, on electrolysing a 10 per cent. solution of zinc sulphate, which contained 0·004 per cent. of

<sup>1</sup> *Zeitschr. f. Anorg. Chem.*, vol. ix., 1895, p. 144.

<sup>2</sup> *Electro-Metallurgy*, 1896, p. 283.

<sup>3</sup> *Loc. cit.*

arsenic as ammoniac arsenite, at the end of a minute zinc sponge was produced. Nahnsen proposes first to precipitate, by means of lime or a similar re-agent, both the zinc and the foreign metals from the crude solutions, and to treat the precipitate thus obtained with the acid electrolyte escaping from the baths. The latter, after it has been neutralised, traverses a series of vessels in which it comes in contact with zinc dust, which precipitates the metals which are electro-negative towards zinc, an equivalent quantity of zinc passing into solution. Iron generally occurs in the neutral or feebly basic solutions as ferrous salt. It can only be precipitated out of the solution after conversion into a ferric salt. According to a patent of the company which has succeeded to Egestorff's Salt Works,<sup>1</sup> iron can be removed from solutions of sulphate by the addition of carbonate of lime, and passing a current of air through the solution. If the iron is present as chloride and not in too large quantity, it is best oxidised and precipitated by the addition of a small quantity of chloride of lime, the calcium chloride so formed having no injurious effect upon the electrolysis. If the quantity of iron present is exceedingly small, the iron is best oxidised by a solution of a chromate and precipitated by the simultaneous addition of soda, zinc oxide or zinc carbonate. Both the iron and chromium are thus thrown down in the form of hydrates, as shown in the following equation, sodium chromate and soda being employed:—



According to Pfeiffer,<sup>2</sup> basic zinc salts ( $\text{ZnCl}_2$ ,  $3\text{ZnO}$ , or  $\text{ZnSO}_4$ ,  $4\text{ZnO}$ ) are to be added to the solutions of zinc to purify the latter and to produce a basic electrolyte, previous to electrolysis. As pointed out by Borchers, when zinc solutions contain ferrous salts, these must be oxidised to ferric salts by means of chloride of lime, sodium hypochlorite, or by chromates before the basic zinc salts are added.<sup>3</sup>

Pertsch<sup>4</sup> assumes that the formation of spongy zinc in the electrolysis of solutions of zinc chloride is due to the formation of haloid acids, oxychlorides, and other imperfectly known compounds. To prevent the formation of sponge, he adds a solution of oxalate in aqueous oxalic acid to the electrolyte. In the presence of this salt the formation of chlorous and hypochlorous acids is said to be prevented, nor is any notable amount of water decomposed. The

<sup>1</sup> D. R.-P. No. 23712.

<sup>2</sup> U.S.A. Pat. 495937, April 19, 1893.

<sup>3</sup> *Jahrb. d. Electro Chem.*, 1895, p. 164.

<sup>4</sup> D. R.-P. No. 66185.

action of the zinc oxalate depends upon the easy decomposability of this salt into metal and acid radical. Oxalic acid used in this process is destroyed in consequence of its decomposition by polarising bodies. Oxalic acid and oxalates have already been used by Classen in electrolytic work, and have proved of service in electrolytic analysis, but they would probably be too expensive on a large scale.

Lindemann<sup>1</sup> has found that a compact and perfectly pure deposit of zinc can be obtained from a solution of zinc sulphate, if zinc sulphide is maintained in suspension in the solution, the sulphide being precipitated by sulphuretted hydrogen from a neutral solution of zinc sulphate. The reactions are expressed by the equations



The sulphuric acid must be rendered harmless by addition of fresh zinc sulphide or of oxidised zinc compounds. Nothing is known as to the application of this process. To prevent the formation of a jagged edge on the cathode (produced by the high current density there) the cathodes are made larger than the anodes. The thickness and the resistance of the electrolyte between the edges of the cathode and anode plates are thus increased, and the current densities on the cathode edges diminished.<sup>2</sup>

We have now to distinguish :—

1. The extraction of zinc from ores.
2. The extraction of zinc from alloys.

### 1. *The Extraction of Zinc from Ores*

When zinc is to be extracted from ores, the solution should, as a rule, be produced apart from the electric circuit. In the majority of the processes proposed up to the present, the zinc is dissolved in the form of sulphate or of a double sulphate, as chloride or a double chloride. Other proposals have been made to dissolve the zinc with sulphurous acid, alkalis or alkaline salts, or with vegetable acids. Unless other metals are to be dissolved from the anodes, it is necessary to work with insoluble anodes. An evolution of gas is thus produced, and a great consumption of electric energy is rendered necessary. At the same time this evolution of gas tends to the formation of spongy zinc. The various depolarising agents will be described under the individual processes to be mentioned below.

A general method of depolarising, proposed by Borchers,<sup>3</sup> which

<sup>1</sup> D. R.-P. Kl. 40, No. 81640.

<sup>2</sup> See Eschellmann, D. R.-P. 117067.

<sup>3</sup> *Op. cit.*, p. 98.

has not yet, however, been employed practically, will alone be referred to here. Borchers proposes, in consequence of certain experiments carried out by him, to employ oxygen separated in the course of electrolysis as an oxidising agent for certain organic compounds in place of the oxidising agents, such as peroxides, permanganates, chromic acid, arsenic acid, &c., hitherto used, and thus to combine the electrolysis of the metal with a process of oxidation to the advantage of both operations. The material for his oxidation process he finds in various distillation products of coal tar, such, for example, as the cresols. By mixing and digesting these substances with concentrated sulphuric acid they are readily converted into cresol-sulphonic acids, which are good conductors and are readily soluble in water. In the course of a sufficiently long-continued electrolysis these are oxidised to carbon dioxide, water, and sulphuric acid. If, however, the electrolysis is interrupted at a suitable time, according to Borchers, the whole series of the theoretically possible intermediate oxidation products can be obtained. It is a necessary condition for the combination of electrolysis with the processes of oxidation that the oxidation product formed shall be readily separable from the solution that has to be electrolysed. In experiments carried out with such materials, Borchers, employing a current of 4.6 to 5.6 ampères per square foot, obtained a brilliant and compact deposit of zinc. In order to maintain this current density, a tension, according to the proportion of zinc in the electrolyte, of from 1.5 to 2 volts was required. When currents of 14 ampères per square foot and an initial tension of 3 volts were employed, Borchers obtained good zinc, but the bath heated rapidly and increased the tension to such an extent that the work became unprofitable. The quantity of zinc which can be calculated upon in this method of depolarisation is given by Borchers as at the utmost 0.9 lb. per hour per horse-power.

The tension required for the decomposition of zinc sulphate is 2.35 volts, and for zinc chloride 2.43 volts, and 1.217 grams of zinc are deposited from zinc solutions by 1 ampère hour.

According to Killiani, the tension, when carbon anodes are used, must be at least 2.5 volts to prevent the deposition of zinc oxide, together with the zinc. Thus 2.5 watt-hours are requisite to furnish 1.217 grams of zinc. The power which is required to precipitate one kilogramme of zinc is therefore 2083 watt-hours, as  $\frac{2083}{736} = 2.83$  h.-p., therefore  $\frac{2083}{736} = 2.83$  h.-p. will be needed. As, however, a horse-power does not produce 736 watts, but from 600 to 680, say

650 watts, in consequence of the power lost when mechanical work is converted into electricity, and as the older dynamos wasted 25 per cent. of the current in consequence of the conversion of the latter into heat, &c., the horse-power must be reckoned as

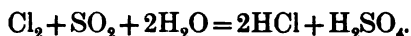
$\frac{2083}{650 \times 0.75} = 4.3 \text{ h.-p.}$  If 2 kilogrammes of coals are reckoned per horse-power per hour, the quantity of coal consumed in the older steam engines using poor coal, for 1 kilo of zinc, would amount to 8.6 kilos. With modern high pressure engines working expansively, and condensing, the coal consumption per horse-power per hour may be taken as 1.5 kilos, so that 6.45 kilos of coal would be needed for the deposition of 1 kilo of zinc.

In the case of zinc chloride solutions the consumption of power would be still greater, since the decomposition tension is higher than in the case of the sulphate (2.43 volts against 2.35), and since the resistance in the bath is greater owing to the need for working with diaphragms. Experience shows that the tension of the bath may be placed at 3 to 3.5 volts. The coal consumption for the distillation of zinc in Belgian and Belgo-Silesian furnaces is less than that required for the electrolytic precipitation of zinc. As regards the extraction of zinc from the ores by means of electrolysis, it is but rarely perfect, as when zinc is leached out by means of dilute acids certain quantities of metal generally remain in the residues. This is especially the case when the ores contain iron, as is generally the case. If ferriferous zinc blende is calcined and then leached out with weak acids, the loss of zinc amounts to 20 per cent. for Upper Silesian ores (Nahnsen). From Rhenish and Belgian ores containing very little iron, zinc is said to be extracted down to 2 per cent., and even less. The presence of lead has no effect upon the extraction of zinc as long as particles of zinc blende are not enveloped in the sulphate of lead formed from the sulphide during calcination.

#### *(a) The Extraction of Zinc from Zinc Ores Proper*

The extraction of zinc from zinc ores proper has up to the present nowhere come into use, and having regard to the power required, as stated above, for the deposition of the zinc, as also for the difficulties connected with the production of compact zinc, there seems but little likelihood of its introduction upon a working scale in the immediate future. The extraction of zinc from solutions of sulphate and chloride, combined with dissolving the zinc out of its ores within the

electric circuit, had been proposed in 1880 by Luckow,<sup>1</sup> but has never come into use upon a large scale. The patent covers the production of zinc by the electrolysis of concentrated solutions, the acids or the chlorine thus liberated being allowed to act upon the zinc ores, whilst polarisation is prevented by mechanical or chemical means. The decomposing cells are to be formed of wooden vats; sheets of zinc are to be used as cathodes, and wire baskets as anodes, these containing mixtures of carbon and zinc ores, or zinciferous metallurgical products, or baskets or boxes made of wire and filled with carbon only. The zinc, which is said to separate out at the cathode in the form of grains, is to be caught on frames covered with cloth, arranged beneath the cathodes. By employing a solution of chloride of zinc or a feebly acid solution of common salt as the electrolyte, and a mixture of coke and zinc blende as the anode, the chlorine evolved during the electrolysis was said to decompose the blende and dissolve the zinc. When the anode consists of carbon alone, the chlorine produced was either to be removed mechanically by forcing in air, or chemically by forcing in sulphur dioxide. This process has not been employed on a working scale. The employment of ores as anodes, or the dissolving of zinc out of them in the bath, causes the liquors to become impure, and baffles all attempts to prepare compact zinc. In the absorption of the chlorine by sulphur dioxide, twice as much hydrogen chloride is produced as is equivalent to the zinc precipitated.



The process of Letrange,<sup>2</sup> which was tested at St. Denis, in France, upon a large scale, depends upon the transformation of zinc blende into the sulphate outside the electric circuit, and the deposition of the zinc from the sulphate by means of the electric current. The ores at St. Denis were blendes, which were exposed to a sulphatising calcination in reverberatory furnaces, or were burnt in kilns, and then brought into contact with the sulphur dioxide produced during calcination. By means of the calcination a portion of the sulphide of zinc was converted into sulphate, another into zinc oxide. By means of sulphur dioxide the zinc oxide was converted into zinc sulphite, which in the course of time was oxidised to zinc sulphate by exposure to the air. The blende thus prepared was transferred to leaching vats, in which it was treated with water or with the acid

<sup>1</sup> D. R.-P. No. 14256.

<sup>2</sup> *Berg- und Hüttenm. Ztg.*, 1882, p. 489; *Dingl.*, vol. cexlv. p. 455; *Austrian Pat.*, November 12, 1881.

solution obtained in electrolysis. The zinc sulphate solution thus obtained was run first into a collecting tank, and thence into the baths. These latter were vats with double bottoms; the zinc solution was introduced into the interspaces between the two bottoms, and rose up through perforations in the upper one. The anodes consisted of plates of carbon, the cathodes of plates of brass or zinc. As it slowly ascended, the zinc solution gave off a considerable portion of its zinc contents to the cathode, and thus reached the upper portion of the tank, whence it flowed through an overflow tube into a collecting tank. From this tank it was made to pass over roasted ore in order to saturate itself with zinc, and was again electrolysed. The arrangement of the plant is shown in Fig. 231. *A* are the vessels for leaching the calcined blende; *B* is the

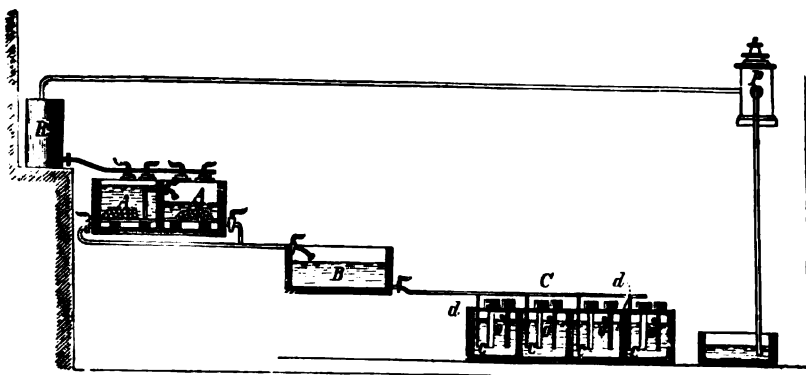


FIG. 231.

collecting tank for the solution; *C* are the baths; *c* are the plates of zinc or brass placed opposite to the plates of carbon forming the anodes; *o* are the openings for the overflow pipes; *d* are the tubes which convey the solution to be electrolysed under the false bottom of the baths. The acid electrolyte is lifted by means of the pump *P* out of the collecting tank placed beneath it into the vessel *R*, from which it passes into the leaching tanks *A*. The zinc is said to have been deposited at the cathode in the form of sheets, and when its thickness reached 0.16 to 0.2 inch, it was stripped off from the cathode by means of a knife. The zinc contained iron, because ferric sulphate was dissolved out from the calcined blende. The current density and tension employed in this process are not stated; as no depolarising took place, these must have been very high. There is no information about the precautions taken to prevent the formation of zinc sponge, nor about the methods of purification. In

the literature on the subject,<sup>1</sup> the amount of zinc deposited per hour per horse-power is given as 1·3 lb., which is far too high a figure. It probably did not amount to 0·4 lb. The fact that this method was given up is proof of its not yielding favourable results.

Hermann<sup>2</sup> has attempted to improve the process by the employment of double salts of zinc sulphate and sulphates of the alkalies, of magnesium or of aluminium. Nahnsen has also recommended the addition of alkaline sulphates to solutions of zinc sulphate; it is, at any rate, a fact that zinc sulphate containing double salts was employed by Nahnsen in his experiments for working the zinc ores at Lipine in Upper Silesia. Nahnsen's process has been tried experimentally at the works of the Silesian Company for zinc mining and smelting in Lipine, but has not succeeded in establishing itself. The composition of the electrolyte is kept secret. It can only be said that it consists of zinc sulphate in combination with other salts which are not decomposed at the tension of the current employed. According to the process patented by Nahnsen,<sup>3</sup> the electrolyte contains 7 to 14 oz. of crystallised zinc sulphate and 1·5 to 3 lb. of alkaline sulphate in the gallon, according to the strength of the current. Nahnsen has communicated the following to the author respecting his process:—

“The ores (blende) are first calcined in the same way as for distillation; they are then brought into contact with hot acid solutions as these leave the baths, the zinc being thus extracted from them. The zinc solution is neutralised and clarified, treated in tanks with zinc dust for the precipitation of any electro-negative constituents that may be present, and then returned to the baths. The essential apparatus in this plant is that used for the solution of the zinc, which is so arranged, upon the principle of opposing currents, that the zinc ores are fed in automatically and the residues free from zinc automatically removed. The whole process consists of the following two phases:—(1) Decomposition of the electrolyte in the bath into zinc and sulphuric acid; (2) transfer of the sulphuric acid or of the acid solution into the dissolving apparatus, where it is saturated with zinc from the ores. It is essential for the execution of the process that solutions free from iron should be obtained. This object is attained by allowing the acid solutions in the dissolving tanks to come in contact with ores containing continually increasing percentages of zinc, so that any oxide of iron in the solutions is rapidly precipitated by the oxide of zinc. By this means solutions of zinc sulphate free

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1883, p. 287.

<sup>2</sup> D.R.-P. No. 24682, April 24, 1883.

<sup>3</sup> D.R.-P. No. 71155.



from iron are obtained. Any electro-negative metals that may be present in the solutions are precipitated by means of zinc dust."

The zinc is obtained pure and in a compact form. With plates 0·8 inch thick, the loss on melting is about 4 per cent. The zinc contains 99·9 per cent. of metal. According to Nahnsen, the question of apparatus is the important one in carrying out this process on a large scale. The process has not yet, however, come into use.

Lindemann<sup>1</sup> proposes to throw down by means of the electric current very pure zinc in the compact condition from solutions of zinc sulphate in which zinc sulphide is suspended. The sulphide of zinc is produced by precipitating a solution of pure zinc sulphate of 37° to 38° B. by means of sulphuretted hydrogen. The electrodes consist of rolled lead. They are 0·4 inch apart, and the current density employed in the experiments amounted to 10 ampères per square foot; the tension, which is not stated, may be taken as 3 to 4 volts. The cathodes were subsequently to be replaced by electrolytic deposits of zinc with their edges cut smooth. The anodes, which gradually become covered with a superficial layer of peroxide of lead, must be freed from the latter by being washed from time to time. As soon as the bath contains 9 to 9½ oz. of free sulphuric acid per gallon, a current density of 10 ampères per square foot can no longer deposit zinc from it. Before, therefore, the free acid present reaches this amount, the electrolyte must be replaced by a neutral solution of zinc sulphate. The zinc sulphide, which is gradually decomposed by the acid liberated, must be renewed from time to time. This process has not yet come into use.

Siemens and Halske<sup>2</sup> propose for the extraction of zinc from its sulphide a process similar to that for the extraction of copper from ores containing copper sulphide,<sup>3</sup> in which polarisation is partly prevented by the secondary action of the anion upon the electrolyte. The slightly roasted zinc blende is to be treated outside the electric circuit with a solution of ferric sulphate containing free sulphuric acid, whereby the zinc is dissolved in the form of sulphate, ferrous sulphate being at the same time produced, and sulphur separated out, two molecules of ferrous sulphate being formed for every molecule of zinc sulphate, as shown in the equation:—



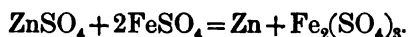
The solution of zinc thus obtained is conducted into the bath, first to the cathodes, and then to the anodes. At the cathodes a portion of the zinc is deposited, whilst the acid radical,  $\text{SO}_4$ , goes to the anode.

<sup>1</sup> D.R.-P., Kl. 40, No. 81640.

<sup>2</sup> D.R.-P. No. 42243.

<sup>3</sup> Vol. i., p. 328.

The solution from which a portion of its zinc has been removed flows to the anode, where the ferrous sulphate is re-converted by the anion,  $\text{SO}_4$ , into neutral ferric sulphate  $\text{Fe}_2(\text{SO}_4)_3$ . This ferric sulphate is then caused to act upon a fresh quantity of sulphide of zinc. By the oxidation of ferrous to ferric sulphate at the anode, an amount of electrical energy equivalent to the heat of combination thus produced is evolved, and this partly counteracts the back electro-motive force produced by the decomposition of the zinc sulphate at the cathode. The process of electrolysis is expressed by the equation:—



This process has never come into use in any way, nor is it likely to be introduced. The solution of zinc sulphide is very slow and very imperfect, and the electrolyte contains very large quantities of iron, which promotes the deposition of spongy zinc. Another proposal of Siemens and Halske,<sup>1</sup> which has likewise failed in practical application, is to treat ores or artificial products containing zinc oxide, in vessels fitted with stirring appliances, with a warm neutral solution of aluminium sulphate, containing 10 to 15 per cent. of  $\text{Al}_2(\text{SO}_4)_3, 18\text{H}_2\text{O}$ . In this way a solution of zinc sulphate and basic aluminium sulphate is formed, and this on electrolysis yields zinc at the cathode and neutral aluminium sulphate at the anode.

Coehn<sup>2</sup> proposes to use accumulator slabs of lead oxide as anodes for the electrolysis of oxy-salts of zinc, such as the sulphate. During the electrolysis, the lead oxide is converted into lead peroxide, and the plates are then to be used for the generation of electricity in lead peroxide and carbon elements with sulphuric acid. Nothing is known as to the practical execution of this process.

The process of Gunnar Elias Cassel and Frederik A. Kjellin, of Stockholm,<sup>3</sup> avoids polarisation by the employment of anodes of metallic iron or of some other metal, a plate of zinc forming the cathode. The anodes and cathodes are separated by a diaphragm of porous clay or some other suitable material. The cathode compartment contains the solution of sulphate of zinc to be electrolysed, which has been produced by the leaching of calcined blende with sulphuric acid. The anode compartment contains sulphate of iron or a sulphate of the metal employed as anode. Zinc is thrown down at the cathode by means of the current, whilst the acid evolved at the anode dissolves an equivalent quantity of iron. The object of the diaphragm is to prevent the intermixture of the solutions contained in the

<sup>1</sup> D.R.-P. 88202.

<sup>2</sup> D.R.-P. No. 79237, 1893.

<sup>3</sup> D.R.-P. No. 67308.

cathode and anode departments. The ferrous sulphate formed at the anode is to be sent into market as green vitriol. This process has not come into practical use because a compact precipitate of zinc cannot be obtained in presence of iron.

Choate<sup>1</sup> proposes the evaporation of very impure zinc sulphate solutions, and the heating of the crystals thus formed in an oxidising atmosphere in a muffle furnace to 250 to 500° C. This treatment is to convert the impurities partly into insoluble compounds, and partly to volatilise them, the zinc sulphate remaining undecomposed thereby. The residue on extraction with water is said to give pure zinc sulphate which can then be electrolysed. Another method of treatment<sup>2</sup> is to electrolyse the impure solutions, using higher current densities than those required to decompose the zinc sulphate, so that the impurities are partly separated at the cathode and are partly precipitated in the bath by secondary reactions.

Solutions of zinc chloride for electrolysis can be prepared by the chloridising roasting of zinc blende, by double decomposition between solutions of zinc sulphate and calcium chloride or sodium chloride in the cold, or by treatment of oxidised ores or roasted blende with hydrochloric acid or ferric chloride. When zinc blende is submitted to a chloridising roasting zinc sulphate is always formed besides zinc chloride. To convert the sulphate into chloride, the solution is treated with calcium chloride, which causes a precipitate of calcium sulphate, and zinc chloride remains in solution. The precipitated calcium sulphate can then be separated from the solution. The production of zinc chloride liquors from zinc ores proper is a costly process, and has therefore not come into practice; their production, however, from pyritic residues, as described later on, has been developed on a working scale, chloridising roasting being employed for the purpose. Zinc sulphate liquors have been converted into zinc chloride by means of calcium chloride at Winnington and Houschau. The chlorine liberated by the electrolysis of zinc chloride solutions can be utilised to prepare chlorine compounds like bleaching powder.

The conversion of zinc into chloride from its ores, and the electrolysis of the solution obtained, has been tried experimentally at Bleyberg, in Belgium.<sup>3</sup> The solution of zinc was produced by treating calamine or calcined blende with hydrochloric acid. Any iron that passed into solution was precipitated by means of chloride of lime. The anodes consisted of graphite or carbon; the cathodes

<sup>1</sup> D. R.-P. 77567.

<sup>2</sup> *Ibid.*

<sup>3</sup> *Berg- und Hüttenm. Ztg.*, 1883, p. 367.

were sheets of zinc. The chlorine evolved at the anode does not seem to have been employed for the manufacture of bye-products; The process was too costly, and had been given up.

Currie<sup>1</sup> proposed to precipitate metals other than zinc at the anodes as insoluble chlorides by the electrolysis of zinc chloride solutions. Höpfner<sup>2</sup> proposes electrolysing in baths partitioned off into anode and cathode chambers by means of diaphragms, the anodes being soluble and of some metal other than zinc. To prevent contamination of the cathode liquor by diffusion from the anode, bodies are added which, combining with the anode metal that has gone into solution, generate the electrolyte at the cathode, and precipitate the anode metal as insoluble salt. Thus lead chloride, by addition of zinc sulphate, gives an insoluble precipitate of lead sulphate, and zinc chloride goes into solution. The double decomposition can be effected either within the bath or outside of it. Zinc acetate may be used instead of zinc chloride as the electrolyte. Nothing is known as to the practical application of this process.

Hintzerling<sup>3</sup> proposes to dissolve oxide of zinc out of calcined blende or calamine or metallurgical products containing zinc oxide, by means of magnesium chloride, and to electrolyse the solution obtained. The zinc is said to be deposited by means of a current tension of 18.5 ampères per square foot from the solution of chloride of magnesium containing zinc oxide; the solution of magnesium chloride, left after the zinc had been thrown down, was to be used for the solution of fresh quantities of zinc oxide. The baths containing zinc were to have been treated with from seven to fourteen times their quantity of magnesium chloride solution, of from 1.26 to 1.29 specific gravity at the boiling point, best under a pressure of 2 to 3 atmospheres, the mass being kept in motion by means of stirrers. This boiling is best carried out in closed vessels, so as to prevent the formation of magnesium oxy-chloride. Any of this substance formed in the solution was to be converted into magnesium chloride by the addition of hydrochloric acid. This process has not come into practical use.

For extracting zinc from pyrites residues the processes to be described below for converting the zinc into chloride and the electrolysis of the solution of chloride, have come into use. Blas and Miest<sup>4</sup> have proposed to crush ores containing sulphide of zinc, and to mould them into plates under a high pressure of about 100 atmospheres with the employment of a temperature up to 600° C.

<sup>1</sup> U.S. Pat. 466720, January 5, 1892.

<sup>2</sup> D.R.-P. 101177.

<sup>3</sup> *Dingl. Journ.*, vol. 288, p. 263.

<sup>4</sup> *Essai d'Application de l'Electrolyse*, Louvain and Paris, 1882.

and to use these plates as anodes in the electric current. For the electrolyte a solution of zinc sulphate, chloride, or nitrate was to be used. This process, which was based upon the conductivity of metallic sulphides for electricity, has not been found satisfactory; the plates, composed of non-homogeneous constituents, must fall to pieces tolerably rapidly in the course of the electrolysis, whilst all action must cease as soon as contact with the conductor is interrupted by the sulphur separated out from the particles of ore nearest to the conductor.

#### *Extraction of Zinc from Solutions of Zinc Sulphite*

Kosmann and Lange<sup>1</sup> propose to treat zinc ores (calamine or calcined zinc blende) with sulphur dioxide and water, and to throw down zinc from the solution of zinc sulphite thus obtained by means of the electric current. The oxygen thereby evolved is said to be absorbed by the sulphur dioxide liberated by the decomposition of the salt, converting it into sulphuric acid. This process is said to require a lower current tension than the decomposition of zinc sulphate. Experiments on a large scale are said to have given 0.4 lb. of zinc thrown down per horse-power per hour. Kosmann states that by the employment of Wolff's locomotive type of engine with condenser the consumption of coal per hour per horse-power amounts only to 2.2 lb., so that these 2.2 lb. of coals are capable of producing 0.4 lb. of zinc. The process has not, however, come into use. Zinc sulphite is soluble in water only as an acid salt, and, when exposed to the air, is converted with tolerable rapidity into sulphate.

#### *The Extraction of Zinc from Solutions in Organic Acids*

This method has not come into use for ores; under this head should be included an English patent of Watt, No. 6,294, 1887, as also the proposal to use acetic or lactic acid as electrolytes.

#### *The Extraction of Zinc from Alkaline Solutions*

The deposition of zinc from alkaline solutions has been repeatedly proposed, but has not come into employment. Kiliani<sup>2</sup> proposes to dissolve zinc from ores and metallurgical products by means of a solution of ammonia or fixed alkali, to which ammonium carbonate

<sup>1</sup> D.R. P. No. 57761.

<sup>2</sup> D.R.-P. No. 29900, March 11, 1884; and No. 32864, August 19, 1884.

has been added, in separate vessels outside the electric circuit, and to electrolyse the solutions, cathodes of sheet zinc or sheet brass and anodes of sheet iron being employed. The zinc is said to be deposited at the cathode in the compact form, whilst a quantity of oxygen, equivalent to the metal deposited, is said to be liberated at the anodes. The solution escaping from the baths is collected in tanks and then pumped back into the dissolving baths, where it dissolves out a fresh quantity of zinc. There are no data with reference to the current density and tension. It is, however, undoubted that with equal current densities the electrolysis of such solutions would require a much higher tension than that of sulphite, sulphate, or chloride; the alkalies are, moreover, dearer than acids. It may therefore be assumed that this process will not come into use.

Höpfner<sup>1</sup> leaches the zinc out of bodies containing zinc oxide (poor zinc and lead ores) by means of an alkaline solution, and conducts this solution to the cathodes of a bath for the deposition of the zinc, chlorine or chlorates of the alkalies or alkaline earths being produced at the cathodes by the decomposition of alkaline chlorides. The ores are ground fine and then brought into intimate contact with alkaline solutions in a dissolving tank provided with a stirrer. Any lead oxide that may be present is dissolved together with the oxide of zinc. After the solution has been freed from foreign metals by means of zinc dust, it is passed in a continuous stream into the cathode division of the electrolytic bath, which is separated from the anode division by a suitable membrane, or pair of membranes with a solution of soda or potash between the two. The zinc produced at the cathode separates out in the compact state, and does so the better the more thoroughly the solution is kept in motion. The anode division must contain a solution of chlorides to be constantly kept at a uniform degree of concentration, and also containing alkaline chlorides, as, for example, solutions of carnallite or of the final liquors of the ammonia-soda process. By means of the electric current chlorine is evolved at the anode whilst the alkalies pass into the cathode division, and unite with the alkali already present there. In consequence of the diffusion of alkalies or alkaline carbonates from the cathode space, oxychlorides are formed at the anode. The chlorine can be collected and used as such, or for the manufacture of bye-products. The evolution of free chlorine at the anodes can be prevented by adding alkaline earths to the solution in the anode compartment, and thus forming chlorates. The solution of chlorates can be worked up for the manufacture of potassium chlorate.

<sup>1</sup> D.R.-P. No. 62964.

W. S. Squire and S. C. Currie<sup>1</sup> have attempted to extract zinc from an alkaline solution of the oxide with the employment of mercury as a cathode. The deposited zinc forms an amalgam with the mercury and is submitted to distillation, whereby zinc is obtained and the mercury recovered.

Burghardt<sup>2</sup> attempts to extract zinc from a solution of sodium zincate, which is to be produced by fusing zinc ores freed from sulphur, such as dead roasted zinc blende, with soda and 3 to 4 per cent. of carbon, and leaching out the molten mass. The ore is to be packed round the anode by means of an asbestos cloth. Its zinc contents are to be oxidised there and thus brought into solution. Strzoda<sup>3</sup> has described a method for the treatment of zinc ores and bye-products containing oxide and carbonate in which the zinc is brought into solution at the cathode, the zinciferous material being so added to the bath that it comes in contact with the cathode. The electrolyte is an alkaline solution and the anodes are insoluble in it. On closing the circuit, hydrogen formed by secondary reaction is liberated at the cathode, and reduces the zinc oxide present there to zinc, which is dissolved in the nascent state by the alkali. From the solution of zinc salt thus obtained the zinc is deposited electrolytically at the cathode. It is not known whether this method has yet passed the experimental stage.

Rontschewsky<sup>4</sup> has sought to combine the precipitation of zinc with the formation of lead peroxide at the anode, by the use of lead anodes and an electrolyte containing anions which form soluble salts on combination with lead, the anions being present in such quantity that but little lead went into solution with the current densities employed. The best salts for this purpose proved to be the chlorates. The lead passing into solution was oxidised quite near to the anode to lead peroxide, the adhesion of which to the anode was prevented by the chlorates. The zinc deposited at the cathode was compact. Using zinc sulphate as electrolyte, the most effective concentration was found to be 7.5 per cent. of  $\text{ZnSO}_4$ , and 0.75 per cent. of  $\text{NaClO}_3$ , and the ordinary temperature was found to be best. The current density was 83 ampères per sq. yard, the tension for solutions containing 7.5 per cent. of  $\text{ZnSO}_4$  was 3.7 volts, and for those with 15 per cent. of  $\text{ZnSO}_4$ , 3.4 volts. With increasing concentration of zinc sulphate, the yield of lead peroxide diminished, and the

<sup>1</sup> English Pat. No. 12249, September 27, 1886.

<sup>2</sup> D. R.-P. No. 49682.

<sup>3</sup> D. R.-P. 118291.

<sup>4</sup> *Zeit. für. Elektro Chem.*, 1900, 7, p. 21, 29; also Borchers' *Elektrometallurgie*, 418.

yield of zinc became smaller with decreasing concentration of the sulphate solution. Diaphragms were found unnecessary, for when the velocity of the electrolyte rose to 2 inches a minute, the lead peroxide still became detached from the anode and fell to the bottom of the bath.

Borchers<sup>1</sup> proposes the treatment of lead peroxide for litharge, lead orange, and other lead pigments containing oxygen.

*(b) The Extraction of Zinc from Ores in which it is a Subsidiary Constituent*

Among the ores which contain zinc as a subsidiary constituent, only zinciferous pyrites residues have up to the present been submitted to electrolytic extraction of the zinc. The extraction of zinc from zinciferous lead and silver ores has been the subject of many proposals, none of which have become definitely established.

Such pyrites residues are the residues obtained in calcining pyrites containing zinc blende, the sulphur of which has been converted into sulphur dioxide and used for the production of sulphuric acid. They consist of ferric oxide, and variable quantities of zinc sulphide, oxide, and sulphate. They can only be used as iron ores when the zinc has been removed from them; as long as they contain zinc they are worthless. In order, therefore, to make these residues valuable as iron ores on the one hand, and for the extraction of their zinc contents on the other hand, electrolytic processes have been proposed, and have been used on a large scale for some time, but have now been given up in Germany (Duisburg, Föhrfurt). In Föhrfurt, Höpfner's method was in practice.

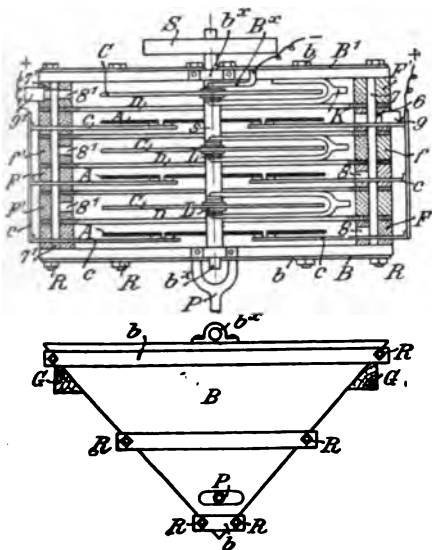
By a chloridising roasting the zinc in the pyritic residues was converted largely in chloride, a little sulphate being simultaneously formed. The roasted mass, which contained, in addition to these two salts, sulphate and chloride of sodium, and salts of iron, manganese, and other metals, was leached with water, and the liquors after settling were deprived of much of the sodium sulphate by artificial cooling. The zinc sulphate and sodium chloride reacted during this process to form zinc chloride and sodium sulphate. After separation of the sodium sulphate the liquors were heated, iron and manganese precipitated by addition of bleaching powder, and other metals more electro-negative than zinc were thrown out with zinc dust. The solution thus purified was then electrolysed in baths, the anode and cathode

<sup>1</sup> *Op. cit.* p. 419.



spaces being separated by diaphragms. The anodes were of carbon, the cathodes were rotating discs of sheet zinc, and the electrolyte was fed in through the bottom of the bath, the nearly exhausted liquid being allowed to flow away at the upper end. Compact zinc was deposited at the cathode, and the chlorine which collected above the anode space was led away by pipes and absorbed by slaked lime to form bleaching powder. The electrolytic zinc was remelted.

The arrangement of a Höpfner bath as used in Fühurfurt for the electrolysis of zinc chloride solutions is shown in Figs. 232-236,<sup>1</sup> Fig. 232 being the end-view of the bath, Fig. 233 the horizontal



FIGS. 232 and 233.

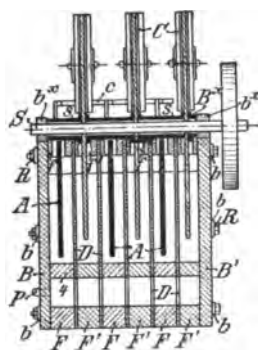


FIG. 234.

section along  $xx$  in Fig. 234, Fig. 234 the vertical section through the middle of the bath, Fig. 235 the front view of a frame of the anode cell, and Fig. 236 the same of the cathode cell. The baths consist of a series of anode and cathode frames made of thoroughly sound wood and bolted closely together. Between these frames are stretched the cloth diaphragms.  $F$  are the anode,  $F'$  the cathode frames,  $A$  the carbon anodes let in through slits in the upper beam  $f$  of the cathode frame, and  $C$  the cathodes let in through corresponding slits  $f'$ . The cathodes are of sheet zinc or iron, and dip to the extent of one-third of their surface in the electrolyte. The anodes are connected to the positive pole of the current through the metallic

<sup>1</sup> *Industries and Iron*, March 18, 1898, p. 208; also Borchers *op. cit.* p. 427.

leads *c* (Fig. 234). The cathodes are attached to the horizontal shaft *S* by the iron strips *L*, which are in metallic connection (Fig. 236) with the negative pole of the dynamo. The shaft rests in two bearings at the short ends of the bath. The electrolyte enters at the bottom of the bath through a pipe with branching nozzles *P* into the channels 2 and 3 of the anode frame and 3' and 2' of the cathode frame.

These channels are formed by the bottoms of the baths 4 and 4' and the dividing partitions 5 of the anode frame and 5' of the cathode frame (Figs. 235 and 236). The electrolyte rises from these channels through the openings 6 and 6' in the anode and cathode frames respectively, it is decomposed electrically on the way, and passes through the openings 8 and 8' in the upper parts of the frames into horizontal channels 7 and 7' and escapes from the top of the bath by

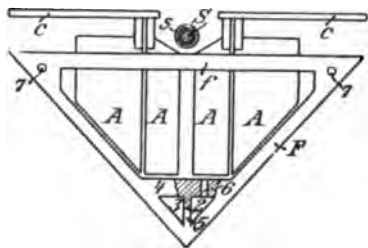


FIG. 235.

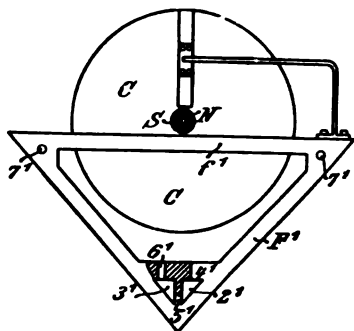


FIG. 236.

the overflow pipes 9 and 9'. The channels are formed by the suitable arrangement of the frames. Between the anode and cathode frames are the diaphragms mentioned above, with the openings requisite for the passage of the electrolyte. The diaphragms are best made of nitrated cloth. The chlorine must be led away from the uppermost parts of the anode cells by pipes (not shown in the figure). The baths may be suspended from beams.

The electrolytic preparation of zinc from solutions of the chloride was introduced into the works of Brunner, Mond and Co., Warrington, England, by Höpfner in 1897, and is still in operation there.<sup>1</sup> The chlorine produced in the reaction is used for the preparation of bleaching powder. The zinc chloride liquors are said to be produced by the aid of calcium chloride, which is obtained as a waste by-product in ammonia-soda process. Zinc and bleaching powder are also produced from zinc chloride solutions at the Alkali Works in Hruschau, near Oderberg, Austria.<sup>2</sup>

<sup>1</sup> *The Min. Ind.*, 1902, p. 267.

<sup>2</sup> *Ibid.*

A method devised by Ashcroft for the treatment of zinc and silver-lead ores at Cockle Creek, New South Wales, was used for a short time, but given up owing to its technical and economic drawbacks. The process consisted in converting the oxide of zinc in the calcined ores into chloride of zinc by means of ferric chloride, whereby the iron was separated as ferric hydrate and mixed with the ore. The ores thus freed from the greater portion of their zinc contents were smelted for argentiferous lead and the zinc precipitated by the electric current from the solution of chloride of zinc, the solvent being at the same time regenerated. Sheet zinc was used for the cathodes, plates of cast-iron and afterwards plates of carbon being used as anodes. The chlorine evolved during the electrolysis combined with the cast-iron anodes to form ferrous chloride solution, whilst where carbon anodes were used it converted ferrous chloride into ferric chloride. Both by the formation of ferrous chlorides, as also by the conversion of the latter into ferric chloride, electric energy was introduced into the circuit. To prevent the deposition of iron at the cathodes the solutions of ferrous and ferric chloride were separated from the zinc chloride by diaphragms of linen, the zinc chloride solution forming a higher column than the solution of the iron salts. From the solution of zinc chloride to be electrolysed first the iron was precipitated, and then the other metals which are electro-negative to zinc, and the solution was conducted first into the cathode department and then into the anode department of the bath, passing first to the iron and then to the carbon anodes. The baths provided with iron anodes formed two-thirds, those with carbon anodes one-third of the total number. The solution escaping from the last carbon anode bath still contained a certain quantity of zinc, and was used for the solution of fresh quantities of zinc oxide from the calcined ores. The baths were arranged in circuit, the electrodes in the different baths being coupled in parallel. The current density amounted to 5 ampères per square foot, the tension in the baths with iron anodes to 1.1 volts, in those with carbon anodes to 2.7 volts. Of the zinc contents of the ore, 66 per cent. were removed by the solution of ferric chloride, which contained 0.8 to 1 ounce of iron in the gallon. The ferric chloride which was lost in the course of the process was replaced by the combination of the chlorine with iron during electrolysis of zinc chloride. Zinc chloride was obtained by decomposing zinc sulphate with common salt, the zinc sulphate being produced by a slow oxidising roasting of ores containing zinc blende. Leaching was a difficult process owing to the slimy nature of the ferric hydroxide precipitated in the mass of the ore; purification of the liquor was

very costly, nor could iron be completely removed from it; the zinc was often spongy, the consumption of energy great, and the residues from the leaching vats, impregnated with ferric hydroxide, could only be further treated with difficulty and great cost. Mention may also be made of the methods of Siemens and Halske, Cowper-Coles, Mohr and Höepfner, for the extraction of zinc from mixed sulphides, though none of these methods has come into use.

The process of Siemens and Halske consists in treatment of unroasted ores with chlorine, whereby chlorides of zinc, silver, and lead are formed, in leaching out with water, which dissolves the zinc chloride and part of the lead chloride but leaves the silver chloride behind, and in the electrolysis of the solution using insoluble anodes and metallic cathodes. Zinc is thus deposited at the cathode, and the chlorine liberated at the anode may be used for the treatment of fresh ore. As the electrolysis must not be carried so far as to completely decompose the soluble chloride, common salt must be added to the electrolyte to keep up the concentration of the combined chlorine. The used electrolyte serves for the leaching of fresh quantities of chlorides.

In the process of Cowper-Coles<sup>1</sup> the finely ground ore is converted into oxide and sulphate by an oxidising roasting, and then lixiviated with water or with a dilute acidified solution of zinc sulphate. This latter operation takes place in vessels fitted with filters, and is facilitated by the passage of an electric current through the acid liquid, insoluble anodes and zinc cathodes being employed. If copper be present in the ores, it goes into solution and is precipitated in vats, the floors of which are covered with a layer of charcoal and iron or zinc. The zinc sulphate solutions are enriched by repeated leaching until they contain 15 to 20 per cent. of the sulphate, and are then electrolysed between lead anodes and rotating cathodes in the form of discs of sheet iron. The ore freed from zinc is repeatedly washed, then extracted with 20 per cent. soda solution, and the alkaline liquor electrolysed for lead. If the object be to prepare white-lead, the alkaline liquor is treated with carbon dioxide under pressure. The residues may be treated for gold and silver by lixiviation with potassium cyanide. Trials with this method have been made at Hayle in Cornwall.<sup>2</sup>

Cowper-Coles<sup>3</sup> has also suggested the sweet-roasting of Broken Hill ores (mixtures of silver-bearing galena and zinc blende),  $\frac{1}{4}$  to  $\frac{1}{2}$  their weight of sulphur, copper, or zinc sulphide being added before

<sup>1</sup> Eng. Pat. 5943, 1898.

<sup>2</sup> *The Min. Ind.*, 1899, p. 747.

<sup>3</sup> *Electric World and Engin.*, 1901, vol. xxxvii, p. 730.

roasting, in order that a porous roasted mass may result. This is then to be extracted with dilute sulphuric acid so as to bring the zinc and copper into solution.

Bernhard Mohr<sup>1</sup> dissolves the zinc from the roasted sulphides by means of sodium bisulphate, and from the solution thus obtained zinc is deposited in the compact form on electrolysis and sodium bisulphate is regenerated.

Höpfner proposes to free the sulphide ores from alkaline earths and soluble sulphides by first extracting with sulphuric or hydrochloric acid, and then to dissolve the zinc by warming the residue gently with a mixture of weak nitric and hydrochloric acids. The sulphur is thus separated in the elemental state, and oxides of nitrogen may be used to regenerate nitric acid. After removal of the foreign metals from the solution, the zinc may be obtained by electrolysis. Another proposal of Höpfner<sup>2</sup> is to digest the silver-bearing sulphide ores of lead and zinc with solutions of cupric or ferric chloride at a temperature of 66° to 88° C. In this way lead and silver are said to go into solution and zinc sulphide remains in the residues. The zinc sulphide can then be converted by suitable means into zinc chloride and the solution of this submitted to electrolysis.

## 2. *The Electrolytic Extraction of Zinc from Alloys*

When zinc alloys are submitted to electrolysis, these form the anodes of the circuit. Both impure zinc, as also alloys of zinc with lead and silver, have been treated electrolytically. The electrolysis of zinc containing lead has been carried out at the works of Aaron Hirsch at Ilsenberg in the Harz, water furnishing the motive power.

Zinc acetate is said to have been used as the electrolyte, and a pure zinc, free from lead, to have been obtained from impure zinc. Nothing further is known of this process. Experiments have been made at the works of the Silesian Company at Lipine to obtain pure zinc from hard zinc (*i.e.* iron-bearing zinc from the refining of zinc) by the method of Nahnsen.<sup>3</sup> The electrolyte was a double sulphate of zinc and an alkali metal, and the anode was made of hard zinc. This, however, was very uneven in quality and could not be improved by re-melting, with the result that spongy zinc was obtained. The experiments have been discontinued. Attempts have also been made<sup>4</sup> to prepare electrolytic zinc from the zinc ashes of the rolling mills.

<sup>1</sup> *The Min. Ind.*, 1899, p. 747.

<sup>2</sup> *Eng. Pat.* 8328, 1895.

<sup>3</sup> *D.R.-P.* 71555.

<sup>4</sup> *Peters, Berg- und Hüttenm. Ztg.*, 1901, p. 601.

These were treated with sulphuric acid, which left the lead behind as insoluble sulphate, and the solution of zinc sulphate was electrolysed after removal of iron by addition of milk of lime and oxidation of the ferrous salt by a stream of air blown through the liquid. This method has not succeeded in establishing itself. Rösing<sup>1</sup> has proposed a process for the electrolytic extraction of zinc from so-called zinc scum, an alloy of lead, silver, and zinc, obtained in desilverisation. This method was tried experimentally for a while at the Frederick Works, in Upper Silesia, but has had to be given up because the distillation of zinc from the zinc scum was found to be cheaper than electrolysis. The zinc is present in relatively small amount, and irregularly distributed in the scum. The latter is also so brittle that it cannot be moulded into plates. Rösing therefore employs the zinc scum in the form of powder, and arranges his electrodes horizontally. Round wooden vats were used as baths. The electrolyte was zinc sulphate: the anode consisted of a plate of lead lying on the bottom of the vat and covered with powdered zinc scum. Above the latter was the cathode, consisting of sheet zinc and supported upon insulators. Several vats were arranged, one above the other, so that the electrolyte could traverse them from above downwards. As soon as the zinc had been dissolved from the grains of the zinc scum to a certain depth, and the contact of the electrolyte with the zinc still contained in the zinc scum was thus gradually diminished, or almost prevented, the scum was removed from the baths and submitted to liquation to free the grains from the crust, which consisted of a mixture of lead and silver, and thus to obtain a fresh zinc surface for the action of the electrolyte. The liquated zinc scum was again submitted to electrolysis, and then again liquated. Liquation and electrolysis thus alternated until the greater portion of the zinc was removed from the scum. The residual argentiferous lead was cupelled. The zinc, which carried both lead and silver, was used for desilvering work-lead. As stated, this process has not come into use.

At Hoboken, near Antwerp, until recently alloys of zinc and silver, which were obtained by desilverising work-lead by means of zinc containing aluminium,<sup>2</sup> were submitted to electrolysis. The anodes consisted of plates of the above alloy; the cathodes were sheets of zinc in the form of discs of 3 feet 3 inches in diameter, which were fastened to a horizontal spindle. This was situated above the surface of the bath, and was revolved so that half of the cathode was inside the solution, the other half outside it. By turning the

<sup>1</sup> D.R.-P. No. 33589; *Preuss. Ztschr.*, 1886, p. 91; *Dingl. Journ.*, 1887. p. 93.

<sup>2</sup> Vol i., p. 916.

cathodes the solution was kept in movement. The electrolyte consisted of a solution of chloride of zinc in chloride of magnesium of a specific gravity of 2.2 to 1.27. After the removal of the zinc from the anodes, these produce a mud consisting of 75 per cent. of silver and 12 per cent. of lead. Experience up to the present has not shown any advantage in electrolysis as compared with other methods of separating zinc from silver and lead. At Hoboken, also, the old process (desilverising with the addition of zinc and distilling off the zinc from the alloy) is now being used. The zinc so obtained is again used for desilverising work-lead. The apparatus of Bridgeman<sup>1</sup> depends upon the principle of keeping the solution in movement by means of rotating cathodes; its construction is shown in Figs. 237 to 240,<sup>2</sup> in which *A* is the tank containing the electrolyte.

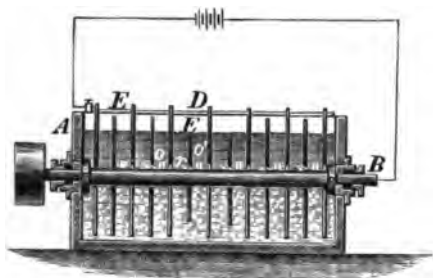


FIG. 237.

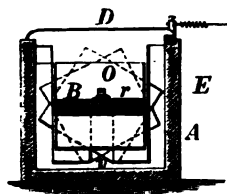


FIG. 238.

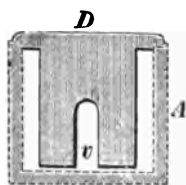


FIG. 239.

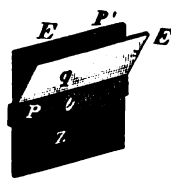


FIG. 240.

Within it rotates the shaft, *B*, protected by an insulator, *r*, and to which the cathodes, *E*, are secured by means of screws and wedges, these screws forming at the same time the connection between the cathodes and the conductors. *D* are the anodes, which are cut out as shown at *v*, so as not to interfere with the movement of the shaft. The detail of the construction of the cathodes is shown in Fig. 240. The sheet metal forming the cathodes, which is coated with graphite, is secured in the frame *p'*, made of non-conducting material. It can

<sup>1</sup> U.S.A. Pat. No. 526482, September 25, 1894.

<sup>2</sup> Borchers, *Electro-Chem.*, 1895, p. 164, Halle, A. S.

be removed from these frames as soon as the deposit has attained the desired density;  $q$  is an opening provided with a locknut,  $q'$ , through which the shaft passes.

Hasse<sup>1</sup> has introduced and carried out the electrolysis of zinc-silver alloys, obtained from the desilverising of work-lead with aluminium zinc, at the Friedrich work, Tarnowitz. The alloy, after liquation to remove excess of lead, contains, according to Roeber:—

Zinc . . . . .	78·64	Lead . . . . .	3·13
Silver . . . . .	11·32	Iron . . . . .	0·24
Copper . . . . .	6·16	Arsenic . . . . .	} trace
Nickel . . . . .	0·51	Antimony . . . . .	

It is cast into anode plates  $\frac{1}{2}$ -inch thick weighing 44 to 66 lb.; the cathodes consist of thin strips of electrolytic zinc, and the electrolyte is a solution of zinc sulphate. The vats are of lead-lined deal 2 feet 6 inches long, 2 feet wide, and 2 feet 4 inches deep, arranged in two rows, each containing 4 vats placed in terrace fashion. Each vat holds 6 anodes and 5 cathodes, the distance apart of these being  $\frac{1}{2}$ -inch. Current is furnished by a Schuckert dynamo at 320 ampères and 15 volts, the current density is 66 to 80 ampères per square yard, and the tension of the bath 1·25 to 1·45 volts. To prevent the formation of spongy zinc, special care must be taken that the electrolyte is pure, and in particular free from copper, arsenic, and iron. Small quantities of suspended metallic particles, *e.g.* of iron, are said to have little or no injurious effect. The electrolyte is purified by being made to flow in a shallow stream over steps placed at the end of each bath. Zinc clippings lie on these steps, and the topmost and bottommost of them form little tanks which contain zinc oxide. In its passage over the steps, the electrolyte is brought into contact with the air, whereby the ferrous salts are oxidised to ferric, and the injurious metals in solution are precipitated by the zinc and zinc oxide. By purification of the liquors in this way, and by causing them to circulate in the baths, the deposition of spongy zinc is prevented when the electrolysis is carried out at 15° to 20° C. under the above conditions of current density and E.M.F. The best density of the electrolyte is 1·4° to 1·6° B. It is kept neutral or slightly alkaline (?), since an acid liquor soon brings about the formation of spongy zinc. (This is not in harmony with the results of the experiments of Mylius and Fromm,<sup>2</sup> who found that the electrolyte must be slightly acid in order that spongy zinc may not

<sup>1</sup> *Zeitschr. für das Berg-, Hütten- und Salinenwesen in Preuss. Staat*, 1897, p. 322.  
Borchers, *Electrometallurgie*, 1903, p. 396.

<sup>2</sup> *Ante*, p. 257.



be deposited.) When Hermann's electrolyte was used (*i.e.*, a double salt of zinc sulphate with sodium, magnesium, and ammonium sulphate) the liquor had less resistance, but the zinc became spongy as the impurities increased.

When the electrolyte was warmed to 60°, the zinc deposited was very porous, and considerable loss resulted on remelting. Cooling to 8° had no influence on the course of the electrolysis. The anodes hang in the baths from 4 to 6 days, the cathodes from 3 to 4. The latter are melted down in iron pots, unless iron-free zinc is required, in which case graphite crucibles are used. The anode mud is removed from the baths weekly or fortnightly. It collects at the bottom of the vat, and the surrounding liquid takes no part in the general circulation. The mud contains lead, copper, zinc, and zinc oxide, besides silver. Zinc and zinc oxide are removed by weak sulphuric acid, and the residue, containing 30 to 60 per cent. of silver, is treated for this metal. This method has been given up.

Waste from the galvanising works, consisting of zinc, crude zinc, zinc oxide, salammoniac, and dirt, may be treated, according to Borchers,<sup>1</sup> by solution of the zinc in hydrochloric acid, and either electrolysis of the purified zinc chloride solution, or evaporation of the same to obtain the solid zinc chloride, which may then be worked up for zinc alloys by the method of Kügelgen. The solution takes place in lead-lined wooden vats; the liquor is neutralised with soda or limestone, and bleaching powder is added to oxidise and precipitate the iron. If but little iron be present, the precipitation is most quickly performed by addition of a solution of a chromate, along with small quantities of soda, zinc oxide, or zinc carbonate. The evaporation of the dilute zinc chloride solution is carried out as in the case of chamber acid in flat lead pans placed one over the other, until a density of 60° B. is attained. Evaporation to dryness is performed in lead-lined cast-iron pots, hemispherical in form, 2 feet 8 inches to 3 feet 3 inches in diameter and 15 to 20 inches deep.

The concentration is carried to such a point that the boiling point reaches 230° to 240° C. Further concentration is not possible, as the lead melts at 300° C. and begins to soften at 250° C. Kügelgen's<sup>2</sup> proposed method, which was mentioned above, consists in melting down the dry zinc chloride with the oxides of other metals and calcium carbide; thus zinc chloride, copper oxide, and calcium carbide give brass. For criticism of this method see Neumann, *Chem. Zeit.*, 1902, xxvi., p. 716—719.

<sup>1</sup> *Op. cit.*, p. 445.

<sup>2</sup> *Zeit. für Electro-Chemie*, 1901, 7, 541, 551, 573.

## THE ELECTROLYTIC EXTRACTION OF ZINC IN THE DRY WAY

Up to the present, it has not been found possible to extract zinc electrolytically in the dry way. Proposals for the extraction of the metal on a large scale in this manner depend upon the electrolysis of molten zinc chloride, or of molten mixtures of zinc chloride with other chlorides, principally those of lead and silver. Electrolysis of molten zinc chloride has been tried on a large scale in England, at Milton. It is essential for this method that the salt should be quite free from water. Lorenz's experiments<sup>1</sup> show that so long as water is present, hydrogen is liberated at the cathode instead of zinc. Melting alone is not enough to drive off all the water; it is necessary to evaporate down with hydrochloric acid. Schultze<sup>2</sup> recommends dehydration by addition of zinc to the molten salt. The action of the metal is facilitated when an electric current is passed through the molten mass, using carbon as cathode and the melted zinc as anode. In this way the water present is electrolysed, the oxygen combines with zinc to form zinc oxide, and the hydrogen is liberated at the carbon cathode. The objection to this process is that the zinc oxide produced dissolves in the chloride forming zinc oxychloride, and this interferes with the subsequent electrolysis, in that a great deal of power is consumed, and but little chlorine, and that mixed with oxygen, is evolved. According to Steinhart, Fox, Vogel, and Fry,<sup>3</sup> zinc chloride can be dehydrated without the formation of oxide or oxychloride of zinc, by heating up to the boiling point of the salt in vacuo, the method of heating and the apparatus being similar to that described for the preliminary dehydration. Borchers<sup>4</sup> proposed to electrolyse fused chloride of zinc between anodes of carbon and cathodes of sheet zinc with current densities of 100 to 200 ampères per square foot of cathode area, and tensions of 3 to 4 volts. He points out that the advantages of this process, which would produce zinc at the cathode and chlorine at the anode, the latter to be utilised in any desired manner, would be that with an equal consumption of power an apparatus for electrolysis would be five to ten times smaller than that required for the electrolysis of aqueous solutions of zinc salts when insoluble anodes are employed, and that chlorine would be produced without the employment of diaphragms. With the above current densities, the tension, even when the current density of the anode is considerably greater than that of the cathode.

<sup>1</sup> *Zeit. für Electro-Chem.*, November 15, 1900, July 4, 1901.

<sup>2</sup> *Zeit. anorg. Chem.*, 1899, vol. xx. p. 323.

<sup>3</sup> D.R.-P. 120970.

<sup>4</sup> *Electro-Metallurgie*, 1896, p. 296.

is said not to exceed 3 to 4 volts. When aqueous solutions of zinc salts and insoluble anodes are employed, this tension is said to be exceeded even when the current density amounts only to 50

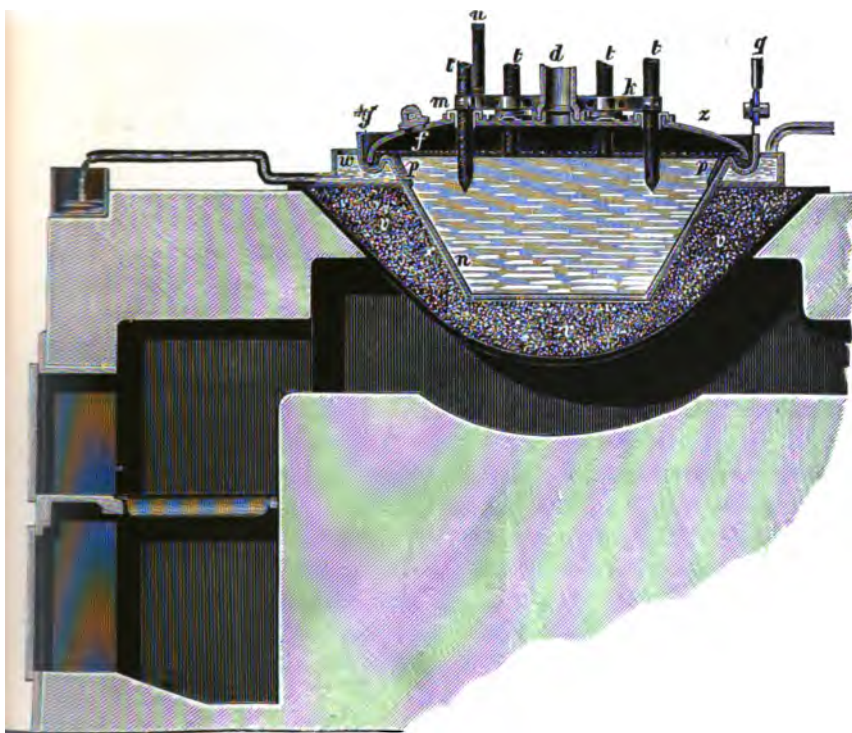


FIG. 241.



FIG. 242

ampères per square foot. Borchers<sup>1</sup> has proposed an apparatus, shown in Figs 241 and 242, for the electrolysis of fused zinc chloride upon a large scale, Fig. 241 being a vertical section through the apparatus, whilst Fig. 242 shows a portion of the cover in plan; *x* is a lead

<sup>1</sup> *Op. cit.*, p. 295.

vessel having the shape of an inverted truncated cone, which has at its upper part a groove, *y*, into which the cover, *z*, fits. A channel, *w*, in which water for cooling the apparatus circulates, surrounds the upper portion of the vessel. The leaden pan is set in an iron pan, *r*, filled with sand, which is heated by means of a grate. The electrolyte is contained in the leaden pan. The anodes are formed by rods of carbon, *t*, inserted through the cover of the pan and connected with each other by means of the annular clamp, *k*, this clamp being connected with the cable, *u*. The individual carbon rods are surrounded by insulators, *m*, where they traverse the cover. The cathodes are formed by pieces of sheet zinc attached to the walls of the leaden pan and connected with the cable, *q*. An opening in the middle of the cover, provided with a tubulure, *d*, serves to conduct away the chlorine evolved during electrolysis, a second opening, *f*, which can be closed when desired, serving for the introduction of the zinc chloride during the operation. The operation is to be conducted as follows:—Chloride of zinc is to be melted in the leaden pan until the molten mass fills the groove, *y*. The cathode, *n*, is then introduced, the cover is put on, and cold water is allowed to flow through the channel, *w*. The cover is kept suspended until a crust of salt, *p*, has formed in the groove and around the upper portion of the pan, when it is allowed to settle down; the current is then passed through, and on account of its great strength, such a quantity of heat is evolved that but little firing is required. The zinc deposits on as much of the cathode as is not protected by the crust of zinc chloride, the chlorine escaping through the tubulure, *d*. Fresh chloride of zinc is added from time to time through the opening, *f*, in order to keep the pan constantly filled with the molten salt. When a sufficient quantity of zinc has been deposited at the cathode, the water current is cut off, so that the crust of salt in the groove, *y*, melts, when the cover can be removed, the cathode with the deposit of zinc taken out, and replaced by a fresh one. Lorenz<sup>1</sup> proposes to submit molten mixtures of the chlorides of zinc, lead, and silver to electrolysis, when lead and silver are said to separate out first, and afterwards pure zinc to be deposited.

Lyte and others have proposed cathodes of molten zinc, and these have found application in the process of Swinburne and Ashcroft. This process has been tried on a large scale at Milton, Staffordshire, and a plant for working it is said to have been erected at Weston Point, England.<sup>2</sup> The ores treated at Milton are mixed sulphides of lead.

<sup>1</sup> *Zeitsch. für Electro-Chem.*, 1895-96, No. 15, p. 318.

<sup>2</sup> *The Min. Ind.*, 1902, pp. 267 and 677.

zinc, and silver. In a paper by Ashcroft read before the Institute of Mining and Metallurgy in London, June 1901,<sup>1</sup> it is stated that the ground unroasted ores (which in the experiments contained 29 per cent. of lead, 26 of zinc, 21 of sulphur, 5 of iron, 2 of manganese, 17 of gangue, and 19 ounces of silver per ton) are charged into a converter containing molten zinc chloride. Chlorine is led in under pressure and this converts the metals into chlorides, with liberation of sulphur. It is said that at temperatures under 600° C. this sulphur forms chloride of sulphur, so that it is advisable to keep the temperature in the converter above 600°, but below 720° C., the boiling point of zinc chloride. The sulphur is collected in condensers, and the zinc chloride, in so far as it is not needed for the fresh charges of ore, is poured or tapped off from the solid residue, which consists mainly of gangue. Of the impurities, iron and manganese are left as insoluble oxides with the gangue, by blowing air through the molten mass at a particular stage in the operations. The molten chloride after leaving the converter is deprived of silver by addition of lead, which takes up the silver, forming an equivalent amount of lead chloride. The silver-bearing lead is removed, then zinc is added to decompose the lead chloride; lead is thus formed and an equivalent quantity of zinc chloride. After tapping the lead, the residual zinc chloride is subjected to electrolysis. The solid residues removed from time to time from the converter still contain large quantities of zinc chloride from which they are freed by extraction with water. The solution thus obtained is evaporated until the zinc chloride melts, the last traces of water along with iron, lead, and other impurities are removed by a short electrolysis with carbon anodes (which are destroyed by oxidation with the oxygen liberated), and the remaining zinc chloride, now pure, is electrolysed along with the chloride from the main reaction.

The electrolysis is performed in a steel vat, 6 feet in diameter, having an 18-inch lining of fire-bricks set in a particular kind of cement. The cathode is formed by a mass of molten zinc weighing 1 ton, metallic connection with the negative pole of the source of electricity being made through a heavy steel block fixed in the lining of the vat, and through five hollow copper leads attached to this block. The anode consists of a movable cast-iron plate, coated on the under side with a special cement, from which 120 carbon rods 10 inches long hang down, dipping 6 inches into the electrolyte. The latter is kept molten by the heat generated by the passage of the current through it. A vat of this sort requires 3,000 to 4,000

<sup>1</sup> *The Electrician*, July 12, 1901.

ampères at a tension of 4 to 4.5 volts, and the output of zinc per week is 1 ton. The zinc is tapped direct from the vat and run into moulds, the vat being then charged with fresh zinc chloride. This is poured into the vat by tipping from a ladle, which is brought into position with a travelling crane. The lining of the vat was not corroded by the electrolyte after a nine-month campaign. The anodes last at least 6 months; the temperature of the vat is kept between 425 and 525° C. Sodium chloride and calcium chloride are added to the electrolyte to increase its conductivity, in such quantity that the percentage of zinc does not exceed 28 (pure zinc chloride contains 48.5 per cent. of zinc). The chlorides thus added are not decomposed by the current, so that they do not need renewing. The chlorine liberated during the electrolysis is drawn into a gasometer by a little ebonite-covered fan, and is there liquefied for convenience in keeping. It serves to produce fresh zinc chloride, being forced for that purpose into the converter under a pressure of 50 lbs. to the square inch. Critical opinion of this process cannot be expressed until the results of longer working on a large scale are forthcoming.

Dorsemagén's<sup>1</sup> experiments have led him to suggest a method for the extraction of lead and zinc from their molten chlorides, prepared from mixtures of galena and zinc blende, which are difficult of metallurgical treatment. The finely pulverised ores are mixed with brine, and treated with electrolytic chlorine in rotating barrels at a temperature of 30° to 40° C. Sulphur separates out, and the lead and zinc are converted into their chlorides, the lead completely, the zinc partially. The chlorides are dissolved by leaching out or by means of hot water, and the residue containing sulphur and zinc sulphide quite free from lead, leaves, after melting away the sulphur, only zinc sulphide, which may be treated for zinc in the ordinary way. If the ores contain silver, the greater part of it is found in the residues, and but a small quantity in the solution. From the solution it is precipitated, and from the residues it is extracted in the course of the treatment for zinc. The solution of the chlorides is now evaporated, the salts are dehydrated and electrolysed in the molten condition in iron vessels, the iron serving as cathode. Liquid lead and zinc collect at the bottom of the bath, and form after a while two layers of zinc-lead alloys, one poor in zinc and rich in lead, the other poor in lead and rich in zinc. These alloys can then be treated for lead and zinc. Experiments with dressed products of Broken Hill ore yielded a residue, after extraction of the chlorides, free from lead and

<sup>1</sup> *Zeits. d. ver. deutsch. Ing.*, 1902, p. 1634; Borchers' *Electromet.* pp. 389, 449.

containing 40 per cent. of zinc and most of the silver. If the mixed ores contain heavy spar, it is advisable to continue the chlorine treatment until all the zinc is converted into chloride. The solution of the chlorides is then treated as above. The dry zinc chloride may also be worked for zinc alloys by melting it with calcium carbide and metallic oxides, as in Kügelgen's method.<sup>1</sup> For a description of the apparatus used in Dorsemagen's trials, and of an apparatus proposed by Borchers for the chlorination, see Borchers' *Electrometallurgie*, page 391.

*The Production of Zinc from Intimate Mixtures of Sulphides of Lead, Zinc and Silver*

Mixtures of silver-bearing galena and of zinc blende free from or containing silver, which cannot be separated by the ordinary methods of dressing, are of frequent occurrence, and form, for example, extensive deposits at Broken Hill, in New South Wales. The treatment of these ores has been the subject of the most varied proposals, without, however, any method becoming established as indubitably the best. Some of these methods have not yet passed the experimental stage, while others have remained mere suggestions. Magnetic separation, like ordinary dressing, has failed to completely separate the galena from the blende. At present most of the ore is dressed in the usual way, and yields considerable quantities of intermediate products which cannot be worked with profit for lead and zinc, along with lead concentrates, which are treated by the roasting and reduction process, the roasting being performed in Ropp furnaces, the reduction in water-jacketed shaft furnaces of rectangular horizontal section.

None of the methods for separating these mixtures chemically, some of which have been considered above, have been quite successful so far. Of the many other methods, some of the best known will now be described.

Fry's method consists in an oxidising roasting of the crushed ores, one quarter of their weight of sulphate or bisulphate of sodium being added towards the end of the operation, so that by its melting the ores are agglomerated. The agglomerated mass is now mixed with  $\frac{1}{2}$  of its weight of ferric oxide (calcined pyrites), and quickly smelted in a shaft furnace, the products being a readily fusible slag and metallic lead (90 per cent. of the ore content), which bears the whole

<sup>1</sup> *Zeit. für Electrochemie*, 1901, pp. 7, 541, 551, 573.

of the gold and silver present in the charge. The slag, according to the latest Patent of H. E. Fry and R. Addie,<sup>1</sup> should be mixed in a finely-powdered condition with a non-bituminous coal or with coke, and smelted in a reverberatory furnace fired by gas, best on the Siemens principle, whereby the reduced zinc is volatilised, oxidised, and collected in towers down which water trickles. The residual slag is tapped. The hearth of the reverberatory furnace is made of burnt dolomite mixed with dried tar when basic slags are to be dealt with, and is separated from the masonry of the furnace by a layer of chrome ironstone rich in chromium. The molten charge is rabbled or poled in order to drive out the zinc as effectually as possible. After an experimental plant at Swansea had treated 20,000 tons of Broken Hill ores by this method, and had yielded 500 tons of zinc oxide (which was sold to the zinc smelters), a large plant was erected at Ellesmore Port, but stopped working as early as March, 1901.<sup>2</sup> In Germany the method has been tried at the Silberhütte, Alexisbad.<sup>3</sup>

The Ellershausen process consists in heating the ores at a red heat in reverberatory furnaces with 50 per cent. of iron or manganese oxide and 25 per cent. of coal. The vapours of lead, zinc, zinc oxide and sulphur dioxide, mixed with the products of combustion, are led into a chamber, where they come in contact with steam and air, forming thereby sulphates of zinc and lead, which are deposited in the chamber. The zinc sulphate is dissolved out from this deposit with water, and the lead sulphate, which contains some silver, goes back into the furnace, where it gives up its silver to the slags. These slags, which contain part of the lead in the charge, are treated as lead ores for lead. The zinc sulphate is treated by some process for zinc, Ellershausen proposing to this end the precipitation of zinc as sulphide with sodium sulphide. In this process the greater part of the silver, along with the gold and copper in the ores and about 2 per cent. of the lead and zinc, are said to remain in the furnace slags. The method has been tried experimentally at Llanelly in South Wales. It has been modified in so far that shaft furnaces have replaced reverberatories, and the zinc is dissolved from the flux dust with sulphurous acid, and precipitated from this solution with sodium sulphide. The sulphide precipitate is filtered in a press and roasted to oxide. At present the smelting is said to be performed in shaft furnaces, ordinary fluxes being used and argentiferous lead obtained. The zinc is obtained from the escaping vapours as sulphide

<sup>1</sup> Eng. Pat. 1898, No. 4911.

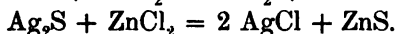
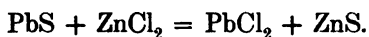
<sup>2</sup> For description of this plant, see Vügel, *Eng. and Min. Jour.*, September 24 1900.

<sup>3</sup> *The Min. Ind.*, 1899, p. 741.

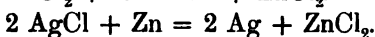
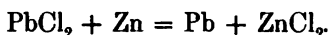


but no longer by means of sodium sulphide, and the zinc sulphide is roasted to oxide; Ellershausen<sup>1</sup> states that 90 per cent. of the zinc content of the ores is obtained from the dust. This method is stated to be in use at Angoulême in France.<sup>2</sup>

In Ganelin's process the powdered ores are treated with metallic zinc, and the molten chlorides of zinc and sodium, in iron vessels fitted with stirring arrangements. The zinc chloride converts the lead and silver sulphides into the corresponding chlorides with formations of zinc sulphide, these reactions taking place according to the equations:—



The zinc sulphide already present in the ores remains of course unaltered. The metallic zinc now reduces the chlorides of lead and silver to the corresponding metals, zinc chloride being formed simultaneously, thus:—



The lead thus produced dissolves the silver and collects at the bottom of the vessel, while the zinc sulphide originally present and formed in the course of the reaction, remains suspended in the molten double salt. The two layers are tapped separately, the argentiferous lead being desilverised by the zinc process, and the double salt and zinc sulphide mixture extracted with water or weak liquor, whereby a solution of the double salt is obtained and zinc sulphide is left as a residue. The zinc sulphide is treated for zinc in the ordinary way, and the solution of the double salt evaporated, the salt dehydrated and used again in the treatment of fresh ore. Nothing further is known of this process, which has been tried experimentally in London.

Suggestions have been made to roast the ores, and then to carry out the distillation for zinc in retorts with basic linings, the residues being treated for silver and lead in shaft furnaces. Thus Sadtler<sup>3</sup> proposes the use of fireproof clay retorts lined with burnt dolomite or magnesite, the same material being also used for coating the most exposed parts on the outside of the retorts. Both lining and coating are to be attached to the retort by a glaze of water glass. There is no definite information about the application of these retorts.

<sup>1</sup> *The Min. Ind.*, 1899, p. 742.

<sup>2</sup> *Ibid.*, 1902, p. 266.

<sup>3</sup> U.S. Pat. No. 656268.

Experiments with them are being tried at the works of the Midland Smelting Company at Bruce, Kansas.<sup>1</sup>

Clancy-Marsland proposes the desulphurising of the ores by heating them with lead sulphate. The zinc oxide thus formed is extracted with sulphuric acid, and the zinc sulphate produced in this reaction is evaporated to dryness and decomposed by heating into zinc oxide, sulphur dioxide, and oxygen. The sulphur dioxide may be worked for sulphuric acid, and the lead-bearing residues smelted. Nothing is known as to the application of this process.

In Neuendorfs method<sup>2</sup> the ores are heated with polysulphates, which are prepared by heating alkaline sulphates with sulphuric acid. This mode of working is said to have the advantage over the method of decomposition with bi-sulphate, in that the high temperature is obviated at which the sulphur of the sulphides is only partly burned to oxide and partly retained by the residues or sublimed; furthermore, this sulphur dioxide, being contaminated with sulphur, cannot readily be utilised. If sodium pentasulphate, prepared by heating 2 molecules of bisulphate with 3 molecules of sulphuric acid, be used, the reaction proceeds as follows (where m stands for zinc, lead, or silver):—



In this way pure sulphur dioxide is obtained along with a melt consisting of 1 molecule of metallic sulphate and 1 molecule of alkaline sulphate. The temperature of reaction is 90° to 100° C. If polysulphate containing less sulphuric acid be employed, sulphur separates out, nevertheless the temperature of reaction is so low that the sulphur neither burns nor sublimes, so that in this case also pure sulphur dioxide is obtained. The sulphur which remains in the residues can be recovered after lixiviation by melting out. Nothing is known respecting the practical application of this process.

G. E. Davis and A. R. Davis propose to extract the zinc along with part of the iron and lead from the unroasted ores by treatment with dilute nitric acid. Lead and iron are to be removed from the solution by addition of zinc oxide, carbon dioxide being passed through the solution to precipitate the lead as carbonate. After evaporation of the filtrate to dryness, the solid zinc nitrate is heated in a muffle to decompose it, the oxides of nitrogen thus produced being worked up for nitric acid along with the nitrous acid produced by the action of the nitric acid upon the ores. This regenerated acid

<sup>1</sup> *The Min. Ind.*, 1902, p. 670.

<sup>2</sup> D.R.-P. No. 103934, December 12, 1888.

<sup>3</sup> *Zeits. für Electrochemie*, 1899, No. 50.

may then be used for the treatment of fresh ore. The residue from the ore treatment contains lead sulphate, silver and gold, and may be smelted for these metals and lead.<sup>1</sup> This method, also, has not found application.

Twyman<sup>2</sup> proposes mixing the pulverised ores with zinc chloride and heating to incipient redness in the absence of air, to convert the lead into chloride and the zinc chloride into zinc sulphide. The lead chloride may be leached out of the mass with water, and the residue, for the greater part zinc sulphide, treated for zinc in the ordinary way. Another method is to roast the zinc sulphide, extract the roasted mass with sulphuric acid, and to precipitate the lead chloride solution with the zinc sulphate solution thus produced. In this way the lead is thrown out as insoluble sulphate, and zinc chloride is regenerated. This process would probably prove too expensive.

Ferraris<sup>3</sup> suggests heating the ores with concentrated sulphuric acid in a furnace, obtaining thereby metallic sulphates, sulphur dioxide, water and sulphur. The sulphur may be burned to dioxide, and this converted into sulphuric acid along with the sulphur dioxide given off in the furnace reaction. The soluble sulphates are leached out of the decomposed ores with water, and the iron oxidised and precipitated by addition of zinc oxide and blowing air through the solution. The zinc sulphate solution thus obtained is evaporated to dryness, and the solid residue heated with coal to convert it into oxide. This method has not come into use.

De Bechi proposes to roast the ores in presence of air and steam, and to pass the gases evolved in this roasting over heated common salt. Sodium sulphate and hydrochloric acid are thus formed, and the latter, after absorption in water, can be used for leaching out the roasted ores. The solution of zinc chloride is precipitated by addition of lime water. Addition of silicic acid to the ores is said to render the zinc more easily soluble in acids. This process is hard to carry out and is expensive.

Picard and Sulman<sup>4</sup> mix the roasted ores with a suitable easily-coking material and some binding substance, and distil the blocks made from this mixture in such a way that a firm coke is first produced, which retains the lead and silver reduced subsequently, whilst the zinc volatilises and is condensed. The distillation residues are smelted in shaft furnaces for silver-bearing lead. This process was first used at the Emu Works in Wales, where 4,000 tons of

<sup>1</sup> *The Min. Ind.*, 1902, p. 676.

<sup>2</sup> *Ibid.*, p. 682.

<sup>3</sup> Eng. Pat. No. 12349, June 17, 1901.

<sup>4</sup> U.S. Pat. No. 665744, January 8, 1901.

Broken Hill ores were treated experimentally, and was then adopted definitely at Cockle Creek, New South Wales. Picard and Sulman state<sup>1</sup> that the ore used in the experiments contained 25 per cent. of zinc and 20 per cent. of lead. After roasting it was mixed with 20 per cent. of coking coal and 5 per cent. of pitch, made into blocks, and these distilled in Belgian furnaces holding 144 retorts, the charge for the whole furnace being 7 tons. Each retort contained 15 briquettes. The coke-like residues, after the distillation of the zinc was completed, contained the reduced lead, the matte, and the slags in the form of fine particles, and the coke was found to prevent the action of the matte and slag upon the walls of the retorts. The residues contained 5 to 8 per cent. of zinc, and the crude zinc contained 99 per cent. of zinc and 0.5 per cent. of lead. The life of the retorts was 35 to 42 days. The loss of lead during distillation was quite inconsiderable. There are no further details about the working of this process.

Schulte<sup>2</sup> recommends distilling zinc ores with coal and a small quantity of tar, asphalt, or some liquid or readily volatile hydrocarbon, so that before the temperature of reduction of zinc oxide is attained, finely divided carbon separates out and envelopes the particles of ore, with the result that the zinc oxide is more effectually reduced, and the slags are prevented from melting together and attacking the walls of the retorts. Much less coal need be taken for reduction when tar is present than when only coal is used. Thus it is stated that reduction is quite as complete when 3 per cent. of tar and 25 per cent. of coal are used, as when 50 per cent. of coal is taken without any tar. The small amount of coal used for reduction purposes in Picard and Sulman's process is probably the result of mixing tar with the charge.<sup>3</sup>

#### *Treatment of Ores containing Zinc for the Production of Merchantable Zinc Compounds*

In many cases ores of zinc are treated in order to produce marketable compounds of zinc, such as zinc oxide, mixtures of zinc oxide, lead oxide and lead sulphate, or zinc vitriol. Such compounds of zinc are, as a rule, only produced when the zinc-bearing ores are not suitable for the extraction of metallic zinc, either because they contain other valuable metals, such as iron, lead or silver, or because

<sup>1</sup> *Dry Process for the Treatment of Complex Sulphide Ores*, Inst. of Min. and Metall., June 19, 1902.

<sup>2</sup> French Pat. No. 318265, January 31, 1902, and U.S. Pat. No. 718222, January 13, 1903.

<sup>3</sup> *Berg- und Hütten-m. Ztg.*, September 19, 1902, p. 482.

they are too poor in zinc. Such ores are more particularly zinciferous iron ores and zinciferous lead or silver-lead ores. The extraction of zinc white is carried on in the eastern United States of North America, especially in New Jersey and Pennsylvania, the production of a mixture of zinc oxide, lead oxide and lead sulphate in the States of Missouri and Colorado, and the production of zinc vitriol at the Julius and Sophia works in the Lower Harz.

### *Production of Zinc White*

Zinc white is produced at the works of the Lehigh Zinc and Iron Company, at Bethlehem, Pennsylvania, at the works of the New Jersey Zinc and Iron Company at Newark, New Jersey, at the works of the Passaic Zinc Company near Jersey City, and at the works of the Bergen Port Zinc Company at Bergen Port, New Jersey. The ore employed for the production of zinc white consists chiefly of a mixture of franklinite and willemite, with variable quantities of calamine and calcite. Zincite, rhodonite and tephroite also occur irregularly distributed in the mass. According to Dürre<sup>1</sup> the franklinite contains 9 to 20 per cent. of manganese, and willemite 2 to 7 per cent., the more rarely occurring rhodonite 42 per cent., and the also scarce tephroite 54 per cent. The average analyses of considerable quantities of these ore mixtures are as follows, according to Dürre<sup>2</sup>:—

	Taylor Mine.				Sterling Hill.	
	1	2	3	4	1	2
SiO <sub>2</sub> . . . .	10·21	11·08	10·33	11·77	4·86	5·15
Fe <sub>2</sub> O <sub>3</sub> . . . .	31·41	27·54	30·36	30·91	30·33	27·62
MnO . . . .	15·84	17·63	15·95	10·27	12·30	13·09
ZnO . . . .	32·83	35·88	26·34	25·71	29·42	23·38
Al <sub>2</sub> O <sub>3</sub> . . . .	0·21	0·24	1·16	2·01	0·67	0·64
CaO . . . .	5·09	2·01	7·15	10·43	12·65	14·37
MgO . . . .	—	0·77	1·09	0·99	—	1·98

The earlier experiments for extracting metallic zinc from these ores failed on account of their high percentage of iron and manganese, by which the retorts were destroyed. On the other hand, the treatment of the raw ores for iron was rendered difficult by the amount of zinc present. An American, Samuel Wetherill, was the first to succeed in treating these ores by employing them for the production of zinc white by means of special furnaces designed by himself. The residues, rich in iron and manganese, which were thus obtained, and which only retain a small quantity of zinc, proved to be a suitable

<sup>1</sup> *Zeitschr. d. ver. deutsch. Ing.*, 1894, p. 185.

<sup>2</sup> *Loc. cit.*

material for the production of spiegeleisen, which is at present extracted from them. Only lately has it been found possible to separate the ores into zinc ores proper, which may be used in the extraction of zinc, and franklinite ores, which serve as raw material first for the production of zinc white, and then for spiegeleisen. This result has been achieved by means of Wetherill's magnetic dressing machine. The ores are crushed in rock breakers down to  $\frac{1}{2}$ -inch diameter, dried in shelf towers, further pulverised and separated into five grades, each of which is dressed magnetically, yielding concentrates of franklinite ores and a mixture of willemite, calamine and calspar. The concentrates are the material used in the preparation of zinc white and spiegeleisen; the other product is further dressed in the ordinary way and yields the zinc ore from which zinc may be extracted. According to Wetherill<sup>1</sup> the ores yield 67·48 per cent. of franklinite ores containing 29·47 per cent. of iron, 13·57 per cent. of manganese and 22·94 per cent. of zinc, and 23·99 per cent. of zinc ores proper, which consist of willemite and calamine and contain 2·2 per cent. of iron, 5·15 per cent. of manganese and 48·96 per cent. of zinc. The franklinite ores average 26 per cent. of zinc oxide, and the tailings contain 4·19 per cent. of zinc. Undressed ores, which used to be worked for zinc white, contained 30 to 35 per cent. of zinc. Wetherill reduces the zinc oxide of the ores in furnaces, the ores lying upon a grate designed by himself, or upon a bed of anthracite resting upon the latter, zinc being thus produced which is burnt to zinc oxide immediately upon its production, by the air and the carbon dioxide contained in the products of combustion. The process is only successful when pure oxidised ores are employed, such as exist in the above-named ore mixtures, when the fuel used is a pure coal burning without the formation of smoke or soot, such as is found in Pennsylvanian anthracite, and when the Wetherill grate with blast in the ashpit is made use of. The zinc oxide intermixed with the products of combustion is cooled down and collected in bags after the zinc has been completely burnt, and particles of coal and ashes have been separated from it, whilst the permanent gases evolved escape through the pores of the bags. As regards the construction of the furnace, and of the cooling and condensing arrangements, the furnace is similarly constructed in all the above-mentioned works, whilst the cooling and condensing plants only differ in unessential details.

The Wetherill furnace, represented in Figs. 243 and 244, consists of an arched chamber provided with doors at either end. Inside it there is a grate, *a*, consisting of a plate of cast-iron 1·4 inches thick

<sup>1</sup> *Eng. and Min. Jour.*, July 17 and 24, 1897.

pierced with conical holes (100 holes to the square foot), the upper smaller end being 0·4 inch in diameter, whilst the lower larger diameter amounts to 1 inch; the grate is supported upon cast-iron bearers. Owing to the conical shape of the holes they are prevented from becoming stopped up. Underneath the grate there is a closed ashpit, *b*, into which air is introduced by means of lateral flues, *c*. The air is forced by means of a fan into a flue running underneath the ashpits of a whole series of furnaces, as shown in Figs. 245 and 246,

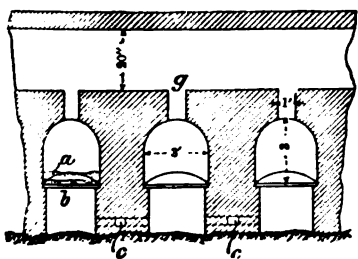


FIG. 243.

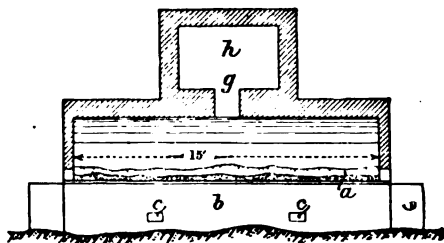


FIG. 244.

in which *C* shows the flue running underneath the furnaces, *A*. From this main flue small flues ascend in the brickwork between the individual furnaces, and these are connected at their upper ends by means of small horizontal flues with the ashpit. These horizontal flues, *c* (in Figs. 243 and 244), can be closed by means of dampers, so as to enable the blast to be cut off from any particular furnace, if the charge in it has been worked off, or for repairs. In the arch above the furnace there are flues through which the gases, vapours and flue dust escape. With smaller furnaces there is only one flue, *g* (in Figs. 243 and 244), to each furnace. Larger furnaces (Fig. 245) have two flues. The gases and vapours pass through these flues either directly into a main flue, *h* (Figs. 243 and 244), or as at the Lehigh Zinc Works (Figs. 245 and 246), first into vertical iron pipes, *B*, and then into a main flue, *D*. The individual furnaces are united to form blocks, which contain up to 34 furnaces (see Fig. 246). The furnaces are either single or double, according as each furnace extends through the whole width of the block or not. The width of the furnaces at the grate is 3 feet; the length of the single furnaces amounts to 5 feet 5 inches, that of the double furnace to 15 feet. The height of the crown of the arch above the hearth is 3 feet. The area of the flue in the arch is about 1 square foot. The doors at the short ends of the furnaces are set in arches 12 inches high and

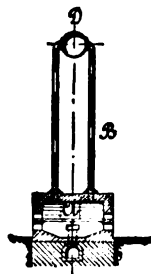


FIG. 245.

32 inches wide. The gases pass through the collecting flues into two towers one after the other, in which, on the one hand, any unburnt zinc vapour is completely burnt to zinc oxide, whilst, on the other hand, any particles of ash or fuel carried off with them are deposited. The towers used at the Lehigh Works are shown in Fig. 246.<sup>1</sup> The current of gases and dust passes through the tube *D* into the tower *E*, being drawn in by means of a fan erected behind the second tower. It then escapes from the bottom of the first tower into the tower *F*, 69 feet high and 79 feet in maximum circumference, which it also traverses from below upwards. Many of the towers are said to contain partition walls also. From these towers the gas current passes into cooling chambers. A fan is arranged between the last tower and

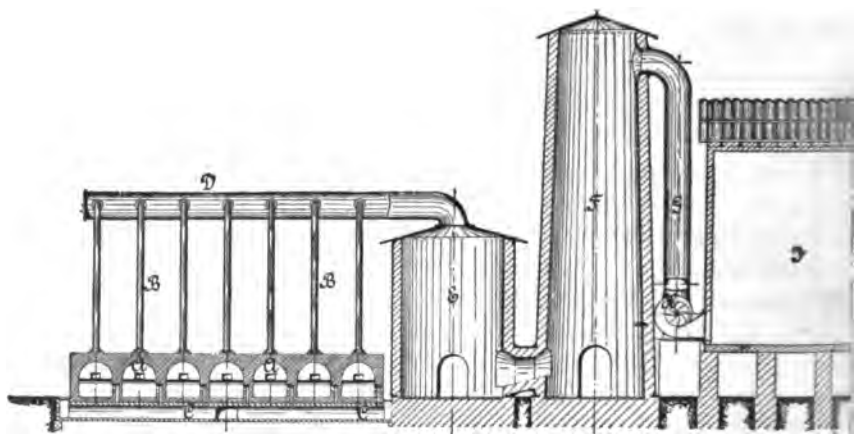


FIG. 246.

the cooling chamber, by means of which the current is driven into the latter. In Fig. 246, *G* is the outlet from the last tower, *H* is the fan, and *J* the cooling chamber. At many works the current is divided between two cooling chambers, which it traverses lengthways. In these chambers the current of gas and dust is cooled down to such an extent that the zinc oxide and gas can be separated from one another in bags of cotton or twill without injury to the latter. The construction of the cooling chambers used at the Lehigh Zinc Works is shown in Figs. 247 and 248.<sup>2</sup> They are 98 feet 6 inches long, 20 feet wide, and 42 feet 6 inches high up to the base of the roof, their walls consisting of polished woodwork, whilst the roof is made of corrugated iron, and the floor, which is formed of sheets of iron, *p* and *q*, sloping towards each other, rests upon supporting walls, *s*. In

<sup>1</sup> Dürre, *loc. cit.*<sup>2</sup> Strecker, *Jahrb. d. K.K. Montanlehranstalten*, 27, 1879.



order to remove the oxide of zinc deposited in these cooling chambers, there are shoots, *r*, in the bottom provided with sliding doors; *x* is a drying floor made of sheet iron upon which the zinc oxide, collected in the cooling chambers, is dried. From the cooling chambers the gas current enters the chambers in which the zinc oxide is caught, the so-called bag chambers. In these the current is distributed through a system of horizontal pipes running near the roof. At distances of 3 feet apart vertical branches descend which have also prolongations upwards. To these there are attached bags or hose 30 to 36 feet long and about 2 feet in diameter, made of strong cotton, which hang down vertically. They are either open below, or else several such sacks are connected together at the bottom in the form of a U. The zinc oxide collects inside these bags, whilst the permanent gases escape through the meshes of the cloth and thus into the open air.

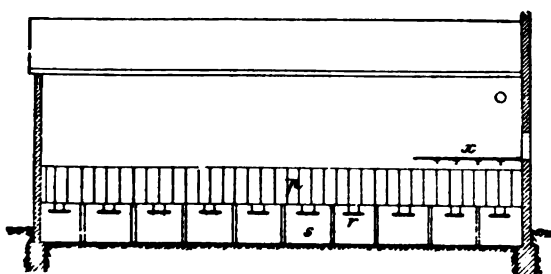


FIG. 247.

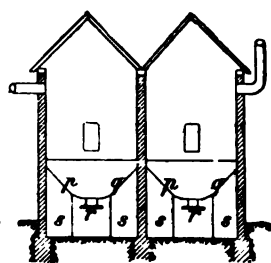


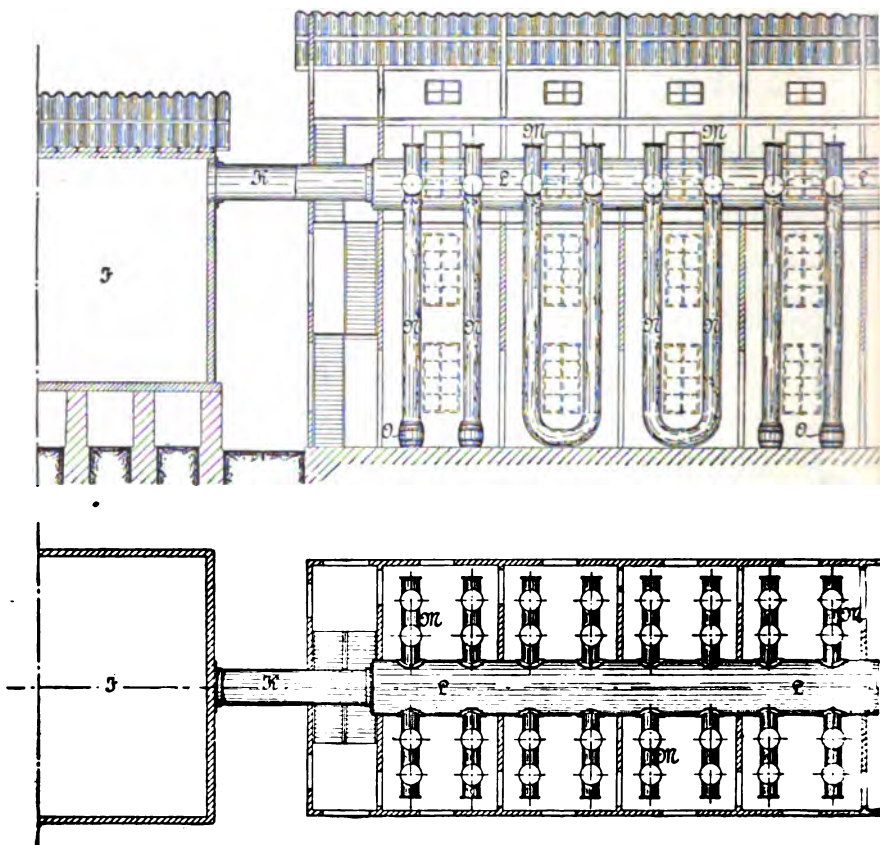
FIG. 248.

The arrangement of these bag chambers at the Lehigh Works is shown in Figs. 249 and 250.<sup>1</sup> *K* is the tube which conveys the current of gas from the cooling chamber, *J*, into the bag chamber. It opens into the main pipe, *L*, 6 feet wide, from which the lateral branches, *M*, open out. *N* are the bags attached to these branches. The topmost portion of the bags has also been made of wire netting for a length of some 6 feet, in order to avoid any injury to the upper portion of the bag by the gases, which are still hot. The open bottom ends of the bags rest either upon the floor or open into casks, in which the zinc white is collected by beating the bags. There are altogether 708 of these bags at the Lehigh Works.

The ore and anthracite are employed crushed to pea size. The grate is first covered with a bed of anthracite, varying in weight between 165 and 200 lbs., according to the area of the grate. The blast is then turned on, and as soon as the layer of coal is thoroughly ignited, a mixture of ore and anthracite is piled upon it.

<sup>1</sup> Dürre, *loc. cit.*

A single furnace is charged with 250 to 300 lbs. of ore and a double furnace with 480 to 520 lbs., anthracite to the amount of 40 per cent. of the weight of the ore being mixed with it. When the furnaces are being regularly worked they remain sufficiently hot after the residues from the treatment of a charge have been removed to ignite the next charge. The air, entering through the holes in the



FIGS. 249 and 250.

grate, burns the anthracite, producing carbon dioxide. This, on its ascent through the layer of anthracite, is partly reduced to carbon monoxide, by means of which gas, as also of the carbon of the inter-mixed coal, the oxide of zinc is reduced to metal. The vapours of the latter are converted into zinc oxide by the action of the oxygen in the excess of air, as also, after partial cooling, by the carbon dioxide contained in the current of gas, and this zinc oxide is carried off by the

gaseous current, passes with the latter through the above-described apparatus, and is finally caught in the bags already described. The time occupied in working a charge depends upon the size of the furnace. At Bethlehem, with a single furnace treating 300 lbs. of ore per charge, it occupies 4 hours; at the Passaic Works, with a charge of 250 lbs., 6 hours. One workman per shift is required for every 4 single furnaces. His duties, in addition to charging and emptying out the furnace, are to keep the charge sufficiently open for the blast to pass through it, and to see that the temperature is maintained. The residues remaining on the grate generally contain from  $2\frac{1}{2}$  to 4 per cent. of zinc, so that the loss of zinc varies from 10 to 20 per cent. of the percentage present in the ore. The proportion of zinc retained by the residues cannot be diminished either by increasing the quantity of coal or by leaving the charge for a longer time in the furnace. It depends solely upon the depth of the layer of ore, and is less the thinner the charge is spread out upon the grate. For instance, in a series of experiments at the New Jersey Works,<sup>1</sup> when the depth of the charge above the grate amounted to between 5 and 8 inches, and the charge was left from 5 to 6 hours in the furnace, the percentage of zinc in the residues was from 1·20 to 4 per cent., whilst when the charge was spread in a layer 12 to 18 inches thick and left for  $13\frac{1}{2}$  to 28 hours, it amounted to 8 to 10 per cent. The residues partly form sintered cakes 2 inches in thickness, partly small pieces and dust. In addition to the constituents of the ore that remain behind, they also contain the ashes (15 to 20 per cent.) of the anthracite, as well as lime, which is in many cases added. According to Dürre, their chemical composition varies between the following limits<sup>2</sup>:—

	Per cent.
Silica . . . . .	18 to 28
Ferric oxide . . . . .	29 „ 36
Alumina . . . . .	2 „ 9
Manganous oxide . . . . .	10 „ 20
Zinc oxide . . . . .	3 „ 15
Lime . . . . .	8 „ 16
Magnesia . . . . .	1 „ 4

The residues obtained at present from the dressed ores (with 26 per cent. zinc oxide) contain in percentages 36·99 of iron, 15·67 of manganese, 15·67 of silica, 4·11 of zinc, and 0·029 of phosphorus.

On account of their richness in iron and manganese they are

<sup>1</sup> Strecker, *op. cit.*, p. 344.

<sup>2</sup> *Loc. cit.*

smelted for spiegeleisen. The zinc oxide is collected in the above-mentioned bags, whilst impure zinc oxide to the extent of 2 to 3 per cent. of the total quantity produced is deposited in the flues, pipes, towers and cooling chambers. The latter is removed from time to time, generally once a week, and is either sent into the market as inferior zinc white or is returned with the ores to the Wetherill furnaces, or is smelted for metallic zinc in retorts. The zinc white deposited in the bags is removed from them by shaking and beating from time to time, generally at intervals of from 2 to 4 hours, and is collected into barrels. If it is damp, it must first be dried upon the drying floor of the cooling chambers and then sifted in a cylindrical sieve, the screening surface consisting of closely-woven linen. At some works, as at Bethlehem, the dried and sifted zinc white, after the casks have been filled, is compressed by means of a press attached to the side or cross-walls of the building, and the cask is then again filled up. The zinc white is sometimes also pressed, first in ordinary sacks, and then packed in casks.

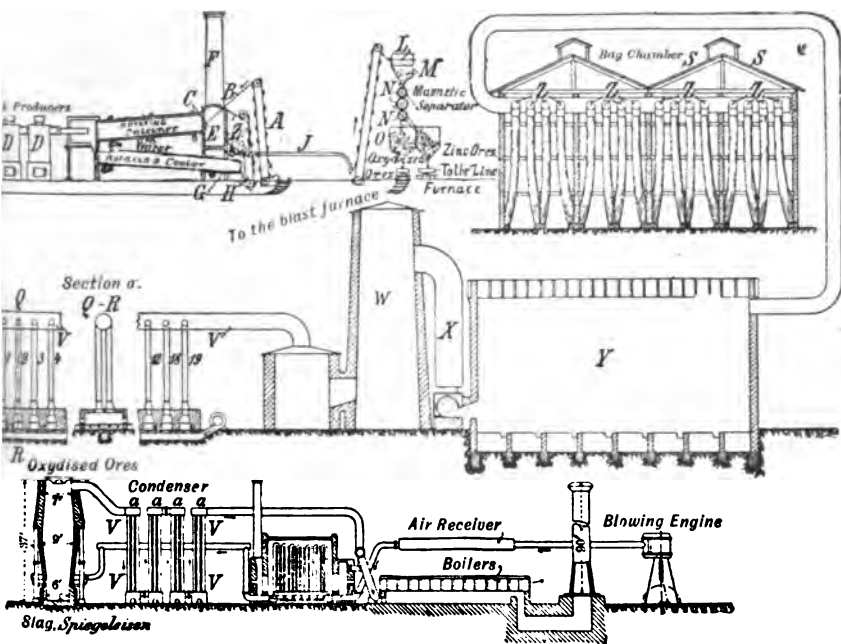
At the works in South Bethlehem, the ore first underwent a reducing calcination in order to convert the iron into magnetic oxide, and was then divided into portions, poor and rich in iron respectively, by means of a Wenström magnetic separator (at present the ore is separated in the unroasted state by means of a Wetherill separator). The portion poor in iron, which contained 46·38 per cent. of zinc, 3·76 per cent. of iron, and 6·68 per cent. of manganese, was smelted for spelter of a high degree of purity known as the Stirling brand, whilst the portion rich in iron, which contained 29·66 per cent. of oxide of zinc, 37·20 per cent. of iron, and 9·34 per cent. of manganese, was first treated for the production of zinc white, and then smelted for spiegeleisen. The reducing calcination was performed in a rotating calciner heated by gas, shown in Fig. 251.<sup>1</sup>

The ore was mixed with 20 per cent. of its weight of anthracite and then introduced into the rotating calciner, *C*, over the sloping surface, *B*, by means of the elevator, *A*. The furnace was heated by producer gas generated in Taylor gas producers, *D*. The ore escaped through the bottom end of the furnace heated to bright redness, whilst the products of combustion escaped at the upper end into the stack, *F*. From the rotating furnace the ores entered the rotating cooler, *G*, through which a current of cool air passed, whilst water was allowed to run over the outside. The cool ore was raised by means of the elevator, *H*, into the hopper, *Z*, and carried by a blast through the pipe, *J*, into a second elevator, which raised it

<sup>1</sup> V. Ehrenwerth, *Mining and Metallurgy at the Chicago Exhibition*, Vienna, 1895.

on to the sieve, *L*, upon which the unconsumed anthracite was retained. The ore that passed through the sieve was transferred to three magnetic separators, *N*, lying one below the other. The non-magnetic portion of the ores from each separator entered the hopper for zinc ores. The separator worked with a current of 50 ampères and a tension of 80 volts, required 20 horse-power to drive it, and treated 40 tons of ore in 24 hours.

The construction of the furnace for the production of zinc white is shown in Figs. 252 to 254, the plant for collecting the zinc white



FIGS. 251-255.

in Fig. 255. The furnace grate is 10 feet long and 4 feet wide. Furnace and ashpits are provided at their short ends with doors, which are kept closed during the operation. From the arch of each furnace two vertical sheet-iron pipes lead into the main pipe, *V*; the latter opens into a cooling chamber, which is connected to the cooling tower, *W*. From this tower the zinc oxide passes into the pipe, *X*, and by means of a fan is forced into the cooling chamber, *Y*, which communicates with the bag chamber, *S*. After the grate has been covered with a layer of anthracite, this is ignited, and then a layer of mixed ore and anthracite, 4·7 to 7 inches deep, is spread over it. The blast

is then introduced, and at the end of 6 hours 83 per cent. of the zinc of the ore is converted into zinc white. A small portion of the latter is collected in the cooling chamber, the greater portion in the bags of the bag chamber. For 100 parts of franklinite 56 parts of coal were employed for admixture and 46 as fuel, the product of the above quantity of franklinite being 24.5 parts of zinc white, containing 99.87 per cent. of oxide of zinc, and 1.5 parts of impure zinc white, containing 99.34 per cent. of oxide of zinc, together with 66.22 parts of residues. The latter were treated for spiegeleisen and zinc oxide. Their composition was as follows:—

	Per cent.
Zinc oxide . . . . .	6.1
Iron . . . . .	38.98
Manganese . . . . .	10.83
Silica . . . . .	19.89
Phosphorus . . . . .	0.026

The residues were smelted in a blast furnace 35 feet high, with hot blast heated to 480° C.; the vapours of zinc escaped from this furnace at so high a temperature that they could not be condensed in the upper portions of the latter. The vapours and gases passed from the blast furnace, as shown in Fig. 255, into an arrangement, *V*, consisting of vertical pipes in which zinc white and metallic zinc were deposited: the gases were then used as fuel for the generation of steam and for heating the blast. To each furnace there were two of these condensers for collecting zinc and zinc oxide, which were used alternately, so that the working of the furnace had not to be interrupted whilst they were being cleaned out; 66.22 parts of residues (= 100 parts of franklinite) yielded 31.72 parts of spiegeleisen, 2.33 parts of impure zinc oxide containing 74.16 per cent. of oxide of zinc, and 57.80 parts of slag, 10 tons of spiegeleisen being produced every 24 hours. For the production of 100 tons of spiegeleisen, 208.6 tons of residues, 114.7 of limestone, and 208.6 of anthracite were required. The greatest works for the preparation of zinc white, zinc and spiegeleisen have been erected recently at Palmerton, Pennsylvania, by the New Jersey Zinc Company. The output per year from this works is estimated at 60,000 short tons of zinc white, 30,000 short tons of zinc, and 72,000 long tons of spiegeleisen.<sup>1</sup> For the preparation of zinc white there are 288 furnaces combined in independent blocks of 12 each.

Zinc white is extensively used in the United States for paint. It has the disadvantage, as compared with the zinc white produced in

<sup>1</sup> *The Min. Ind.*, 1892, p. 663.

Europe by the combustion of zinc, that it becomes slightly yellow in time. Zinc white is produced from zinc blende in the same way as it is from ores containing franklinite. If this blende is not dead roasted, the zinc oxide will contain some sulphate. At Bergenport the charge consists of 645 lbs. of calcined blende, and 300 lbs. of anthracite. Gray oxide of zinc has also been produced in this way in Europe. In Swansea, England, and in Belgium, calamine and the dressed residues from distillation vessels have been similarly treated for zinc oxide. If the ores contain galena, sulphate of lead and oxide of lead are also formed, these bodies likewise passing into the zinc white.

Plant was erected at Joplin, Missouri, in 1901, for the preparation of zinc white from carbonate containing 37 per cent. of zinc.<sup>1</sup> Middleton<sup>2</sup> has proposed to use a reverberatory furnace without fire bridge for the preparation of zinc white from ores. The ore consisting of roasted blende or calamine is first heated on the hearth of the reverberatory and then raked on to the full-charged grate. The reduced zinc burns and is drawn over the hearth into condensers. The ashes from the fuel are removed by turning the movable grate.

The preparation of zinc white by electrothermic methods has been introduced at Crampagna, Ariège, in France.<sup>3</sup> The vapours of zinc and carbon monoxide, obtained by reducing calcined calamine or zinc blende in the electric furnace, are mixed with air and burnt. The carbon monoxide burns to dioxide, and this exerts an oxidising action on the zinc. The complete combustion of the zinc takes place in a chamber into which the vapours are led and from which they escape through iron pipes into cooling chambers, where the greater part of the zinc oxide is precipitated. From these they are drawn by a fan and filtered through bags, which retain the zinc oxide and allow the gases to escape through the pores of the cloth. The zinc white obtained in this way is said to have great covering power; the impurities consist to the extent of 5 per cent. of silica, alumina, lime and lead oxides, and the amount of lead should not exceed 1 per cent. According to Salguez the yearly output is 1,000 to 1,500 tons with a consumption of 500 to 1,000 h.p.

#### *Preparation of Mixtures of Oxide of Zinc, Sulphate of Lead and Oxide of Lead*

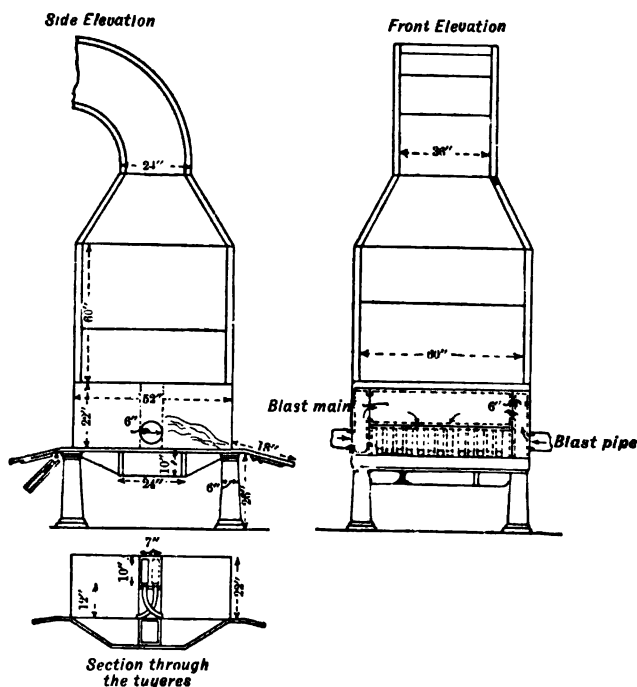
At various works the zinc is removed from lead ores containing zinc by reduction of zinc oxide and oxidation of the escaping zinc

<sup>1</sup> *The Min. Ind.*, 1902, p. 674.

<sup>2</sup> Eng. Pat. No. 12274, June 15, 1901.

<sup>3</sup> French Pat. No. 318265, Jan. 31, 1902 U.S. Pat. No. 718222, Jan. 13, 1903.

vapours. The zinc oxide thus formed, which always contains considerable quantities of lead sulphate and lead oxide, is collected and sold as a paint. If the ores contain silver, a portion of the silver always passes off with the oxides. This process is carried out in reverberatory furnaces and in hearths. It is in use at Joplin, Missouri, and at Cannon City, Colorado, and is known in these places as the Bartlett process. At Joplin, Jasper County, Missouri,<sup>1</sup> the ore consists of blende containing galena with 70 to 73 per cent. of lead.



FIGS. 256—258.

It is treated in double hearths cooled by air and water, the construction of which is shown in Figs. 256 to 258, with the addition of 2½ per cent. of lime, the first products being lead, zinciferous lead, fume and slag. The hearth rests upon cast-iron columns, so that its lower portion is cooled by air. The hearth space is divided by a hollow cast-iron block, lying on the bottom, into two portions, each of which forms a separate hearth, and can be worked independently of the other. This partition forms the back wall common to both furnaces.

<sup>1</sup> Davey, *Trans. Am. Inst. Min. Eng.*, vol. xviii, p. 674; Clerc, *Eng. Mag. Jour.*, July 4, 1896; Ramsay, *Scientific American*, Supplement, May 14, No. 593, 1887; *Trans. Am. Inst. Min. Eng.*, February, 1889.



and has an opening in the lower portion, through which it fills with molten lead. Upon it lies a hollow cast-iron water box in which water circulates, and above this is an iron air box divided lengthways into two portions, in which air circulates. Through both divisions of the air main the blast passes into a row of copper tuyeres, seven for each division, which pass through the water box and convey the blast, heated in the air box, into the hearth. By means of the blast, a portion of the galena is converted into lead sulphate and lead oxide, which bodies combine with the undecomposed sulphide of lead to form metallic lead and sulphur dioxide. A portion of the lead is volatilised and oxidised by the blast; a portion of the lead sulphide is also volatilised and converted by the blast into sulphate. The sulphide of zinc is first converted into zinc oxide, which is reduced by the fuel, the blast converting the zinc vapour again into oxide. The lead and zinc fume is cooled, and then collected in woollen bags, forming a gray powder. By burning out the carbonaceous substances, particles of soot and coal, contained in it, it is converted into white crusts, which are smelted with the slag obtained in smelting the galena, in low blast furnaces with coke at a very high temperature. An additional row of tuyeres is provided in the upper portion of the blast furnace for the oxidation of the volatilised lead and zinc. Lead, slag and fume are thus produced. The last-named is first cooled, and then collected in bags, and forms a white product, saleable as paint. Its composition is shown in the following analysis:—

	I.	II.
PbSO <sub>4</sub> . . . . .	65·46	65·00
PbO . . . . .	25·85	25·89
ZnO . . . . .	5·95	6·03
Fe <sub>2</sub> O <sub>3</sub> . . . . .	0·03	0·02
CaO . . . . .	0·02	0·02
CO <sub>2</sub> . . . . .	1·53	2·00
SO <sub>3</sub> . . . . .	0·04	—
H <sub>2</sub> O . . . . .	0·69	0·85
Insoluble . . . . .	0·08	0·08

In the hearth described above 13½ tons of ore are treated in 24 hours with a fuel consumption of 13½ tons of coal.

At Cannon City, in Colorado, the Bartlett<sup>1</sup> process is in use for the treatment of mixed galena and blende containing noble metals, the object being to convert the lead and zinc into a mixture of lead sulphate and zinc oxide, and to concentrate the noble metals in a cupriferosus matte. The ores are treated according to their content of zinc. Those with more than 20 per cent. of this metal are roasted

<sup>1</sup> Hofmann, *The Metallurgy of Lead*, p. 138.

with blast in sintering or blowing up furnaces, and yield thereby a sintered mass of lead and matte, which is further treated for flue dust and matte in shaft furnaces, the greater part of the zinc and nearly all the lead being volatilised in the sintering furnace; ores with less than 20 per cent. of zinc are treated directly for the dust and matte in shaft furnaces, or are worked along with sintered ores for the same products.

The sintering furnace is shown in Figs. 259 and 260. The grate, only half of which is visible in Fig. 259, consists of two step grates, *a*, and a horizontal grate, *b*, the total length being 6 feet, and the breadth  $3\frac{1}{2}$  feet; one end rests on side walls of the furnace, over which rises an arch; *c* is the ashpit closed by the door *f*, *h* the working door, *g* the flue for the escape of gases and solid particles blown away by the blast. The side walls of the arch rest upon hollow iron pillars, *k*. These have been lately supplanted by water jackets. In the pillars

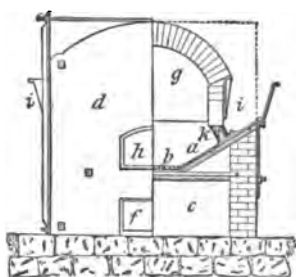


FIG. 259.

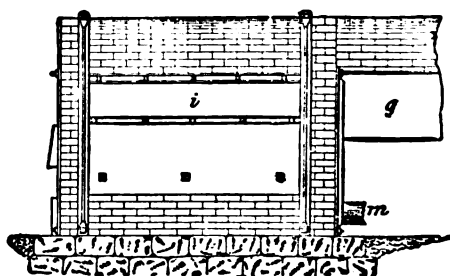


FIG. 260.

are openings on the side facing the furnace, which serve for the admission of compressed air to the charge. The materials are charged through the hopper, *i*, and fall between the pillars, *k*, on to the grid. The blast is conveyed along the pipe, *m*, and is directed into the charge through the hollow pillars and the grates. The ore is charged in with 15 to 20 per cent. of slack coal, the coal becoming coked in the lower part of the hopper and in the upper layers on the step grate. When the charge has reached the horizontal grate it is spread out 6 inches thick by a workman, operating from the working door, and the empty hopper is then refilled. The blast is then turned on. The coke is kindled in the furnace which is still red hot from the treatment of the previous charge, and the flames, at first blue from the burning carbon monoxide, turn white when the zinc and lead volatilise. After 30 minutes' working, practically all the lead and most of the zinc is driven out; the sintered mass of matte

and slag, known as clinker, which remains is then raked out and the furnace is charged afresh. The blast pressure is 4 to 8 ozs. per square inch; 6 tons of ore are worked off in 24 hours, and one man attends two furnaces. The clinker contains:—

	Per Cent.
Ferrous oxide . . . . .	30 to 50
Silica . . . . .	27 „ 31
Sulphur . . . . .	7 „ 11
Carbon . . . . .	3 „ 3.5
Zinc . . . . .	10 „ 20
Copper . . . . .	0 „ 2
Lead less than 1 per cent.	

The matte contains most of the gold and silver.

To obtain the zinc and the matte from the clinker, it is smelted in a low shaft furnace with ores containing less than 20 per cent. of zinc, sulphides of lead, zinc and copper, lime and quartzose ores being added in such quantity that the charge contains (besides silica and iron) 17 to 20 per cent. of zinc,  $2\frac{1}{2}$  to 4 of copper, 3 to 10 of lead, 15 to 20 of sulphur, and 10 of lime. The coke added amounts to 6 to 15 per cent. of the weight of ore, varying according to the zinc content. The arrangement of the furnace used is shown in Figs. 261 and 262. The horizontal section is rectangular, and measures 108 by 36 inches. The foundation walls are shown at *a*; *b* is the blast pipe which enters a wind chest, the blast reaching the charge through openings, *c*, in the chest, 8 by  $1\frac{1}{4}$  inches in size. For the purpose of warming the blast, the pipe, *p*, is led along the dust flue. The water jacket is at *d*, the inlet pipes for the water at *e*, and the outlet pipes at *f*; *g* are the charging hoppers, *h* the shaft, and *k* the flue through which the dust and vapours from two furnaces escape into cooling chambers. The slag is run off into slag pots along the gutter, *m*, the bed of the furnace sloping towards this gutter so that the slags can be tapped directly. The blast pressure amounts to 12 ozs. per square inch. The furnace works off 40 to 75 tons of charge in 24 hours, the quantity varying with the zinc content, being 40 tons when the zinc content is 20 per cent. and 75 tons when 12 per cent. Three men attend a furnace per shift. After four weeks' furnace campaign the dust flues must be cleaned out. The output of matte from 10 to 12 tons of ore is 1 ton, and this averages 40 per cent. of copper and 125 and 2 ozs. per ton of gold and silver respectively.

The slags may contain up to 15 per cent. of zinc oxide, though

they should not average more than 7 to 8 per cent., otherwise the slags retain silver. The silver content of the slags is 0.25 to 1.25 ozs. per ton, and is smaller the greater the quantity of lime present. Basic ferri ferrous slags dissolve 20 to 25 per cent. of zinc oxide. Lime in the slags in quantities up to 15 per cent. is necessary for the solution of zinc oxide; more than this amount, however, hinders the solution of zinc.

The vapours from the sintering and blast furnaces are drawn by a fan into a mixing and cooling chamber, cooling being promoted by the admission of air, and a uniform temperature being attained. They pass thence into a sheet-iron chamber, entering at the bottom

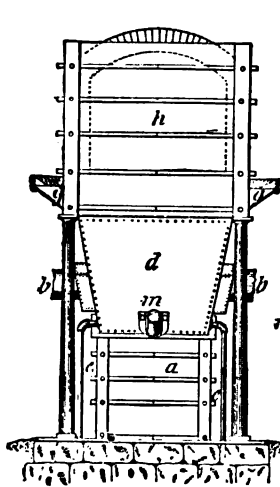


FIG. 261.

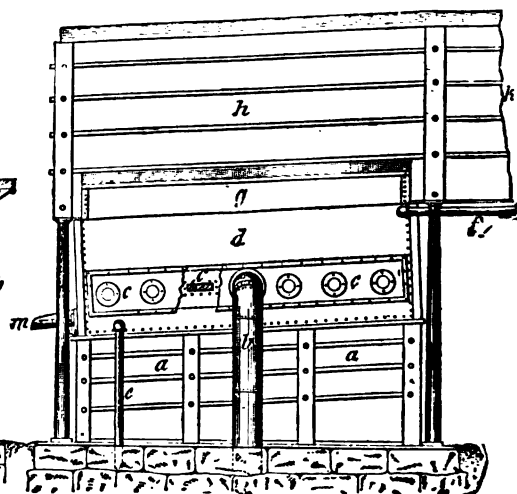


FIG. 262.

and striking the top. A considerable amount of flue-dust is deposited in this chamber, but the greater part settles down in the next two cooling flues, which are each 1,480 feet long and 8 by 3 feet wide. The flue-dust is removed from these through side doors. For 1 square foot of grate area in the sintering furnace, 25 square feet of cooling flue surface is reckoned. From the flues the vapours pass into sacks which further separate the gases from the dust. The sacks are made of cotton or wool 21 feet long and 20 inches across; the cotton ones last 18 to 24 months, the woollen ones 6 to 10 years. The temperature of the room must not exceed 90° and 120° C. when the bags are of cotton and wool respectively. For 1 square foot of grate in the sintering furnace, there are needed 200 square feet of wool or cotton. If twice shaken in 24 hours 1 square yard of wool

yields 1 lb. of dust; and 1 square yard of cotton  $\frac{3}{4}$  lb. The flue-dust contains 12 per cent. of lead sulphide, 30 of lead sulphate, 14 of zinc oxide, 40 of zinc sulphite, 1 of carbon, 1 of silicon, and 2 of sulphur dioxide. The flue-dust from the sintering furnace contains 4 ounces of silver per ton and that from the shaft furnace 8 ounces per ton. The silver losses are given at  $\frac{3}{4}$  ounce per ton when the copper content exceeds 4 per cent., and 3 ounces per ton when 1 per cent. of copper is present. The loss of zinc is 5 per cent., but the lead shows a slight excess over the dry assay.

The coarse flue-dust is converted into a mixture of zinc oxide and lead sulphate by heating it in cast-iron cylinders. These cylinders, of which there are two in a furnace, are 10 feet long and 1 foot in diameter, and are fitted inside with a transport screw. Four iron bars equally spaced and running the length of the cylinder, serve when the screw is rotated to lift up the dust and allow it to slip back. Air enters the cylinder at the top end through a circular opening, and escapes at the lower end through a vertical pipe. This pipe fits into a horizontal sheet-iron cylinder, in which any dust carried over settles out, and from which the gases escape into the open through an upright lead pipe. The screw forces the dust from the back to the fore-end of the cylinder, crushing it at the same time, and any carbon and foreign volatile metals like arsenic are oxidised by the instreaming air and carried away. The temperature of the cylinder is kept at 815° C., and the flue-dust takes 20 minutes to traverse the cylinder. When it emerges it falls on to a small transport screw which carries it to a sieve upon which the coarser portions remain. A cylinder puts through 1,200 to 1,500 pounds of flue-dust daily, and 5 measures of raw flue-dust yield 1 measure of refined dust or pigment containing 47·33 per cent. of zinc, 24·92 of lead, 2·96 of sulphur and 24·34 of oxygen. It consists chiefly of zinc oxide and lead sulphate and is bluish-white in colour. One ton of ore requires for treatment 3·25 H.P. and 0·75 man. Roasted zinciferous lead and silver ores used formerly in Freiberg to be smelted in reverberatories with coke, and the reduced zinc volatilised and collected as zinc grey. This process has, however, been discarded owing to the disadvantage attending it in the volatilisation of lead and silver.

#### *The Production of Zinc Vitriol*

At the Herzog Julius Works, at Goslar, and at the Sophia Works, near Langelsheim, zinc vitriol is produced from the lead ores of

Rammelsberg, which contain considerable quantities of zinc blende. These ores consist of:—

	Per Cent.
Galena . . . . .	9 to 12
Zinc blende . . . . .	27·5 to 30
Copper pyrites . . . . .	1 to 1·69
Iron pyrites . . . . .	11 „ 16
Gangue . . . . .	44 „ 47

The average content of sulphur and metals in the last few years may be taken as:—

	Per Cent.
Sulphur . . . . .	16 to 18
Silver . . . . .	0·001 „ 0·005
Copper . . . . .	0·45 „ 0·55
Lead . . . . .	9·98 „ 10·5
Zinc . . . . .	18 „ 19·5
Iron . . . . .	5 „ 7

The gangue consists chiefly of barytes. The ores are calcined three times in heaps, by which a portion of the sulphide of zinc is converted into sulphate. The latter is more especially contained in the small ore, which is therefore removed after each fire. The first fire lasts for 6 or 7 months, heaps of 500 tons being treated; the second and third fires are given in calcining houses, the heaps being left uncovered. Each heap contains up to 2,000 tons of ore. The second fire lasts 6 to 8 weeks; the third, 4 to 6 weeks. The small ore separated after the various fires contains the zinc partly in the form of neutral zinc sulphate, partly as a basic sulphate and oxide. The neutral sulphate is brought into solution with water, the basic sulphate and part of the oxide with weak sulphuric acid. The small ore and the roasted lump ore have the following average composition:—

	Small Ore. Per Cent.	Lump Ore. Per Cent.
Ag . . . . .	0·015	0·013
CuO . . . . .	1·34	0·93
PbO . . . . .	14·44	10·02
ZnO . . . . .	19·12	28·14
Fe <sub>2</sub> O <sub>3</sub> . . . . .	22·95	13·64
SO <sub>3</sub> . . . . .	15·95	16·62
S . . . . .	0·60	0·17
Insoluble residue, alkaline earths, CO <sub>2</sub> , H <sub>2</sub> O, traces of Mn . . .	8·505	—
Heavy spar . . . . .	—	24·66
Gangue . . . . .	—	5·81

In order to remove the neutral zinc sulphate, the small ore is systematically leached with water and waste solutions, and after being dried in reverberatory furnaces is smelted for lead, together with the lump ore from the third fire, in blast furnaces. The small ore is leached in horizontal cylindrical drums driven by machine power. The ends of these drums are made of cast iron, the sides of wrought iron. Their length is 3 feet 11 inches and their diameter 3 feet 3 inches, and they contain from 1 to  $1\frac{1}{4}$  tons of ore. The ore is leached four times, the two first times with the unsaturated solution ( $10^{\circ}$  to  $15^{\circ}$  B.) from a previous operation, the two last times with hot water, yielding thereby solutions of density  $15^{\circ}$  and  $10^{\circ}$  B. respectively. These are used for preliminary leaching as mentioned above. The small ore from the third fire contains much basic zinc sulphate, so that at the Sophia Works sulphuric acid is added to the leaching liquor. At the Julius Works the roasted smalls from the third fire are steeped in sulphuric acid ( $20^{\circ}$  B.) in a lead box, and then leached out with pure water. In this way the basic sulphate and part of the oxide are brought into solution. The drums make 25 revolutions per minute. The first solution of  $50^{\circ}$  B. and the second of  $20^{\circ}$  B. are mixed so as to form a lye of  $30^{\circ}$  B., clarified, freed from iron and sulphate of lime, and then evaporated down to the crystallising point, when the zinc vitriol is allowed to crystallise out. The solutions are clarified first in wooden troughs 30 inches broad and 22 inches deep, and then in brick tanks lined with cement, 10 feet long, 4 feet 3 inches broad, and 3 feet 3 inches deep. These tanks are provided with a wooden grating, upon which there is a layer of the richest small ore. The solution is thus further concentrated by being allowed to filter through this layer. The clarifying of the solution consists in heating it for 24 hours to a temperature of  $80^{\circ}$  to  $90^{\circ}$  C., in pans made of sheet lead 0.5 inch thick, 13 feet long, 10 feet broad and 2 feet deep, which stand upon a cast-iron plate, and are surrounded with a brick wall one brick in thickness. The solution is then transferred to wooden boxes lined with sheet lead, 10 feet long, 7 feet 3 inches broad and 3 feet 3 inches deep, for a period up to 10 days. The iron is converted by the heating into a basic sulphate, and separates out together with the sulphate of lime and other sparingly soluble bodies, in the tanks. About half a ton of coal is required for the clarifying of 255 cubic feet of solution of  $30^{\circ}$  B. The solution thus purified is evaporated in pans similar to those used for clarifying, down to  $50^{\circ}$  B., and is then run out into cooling vats made of wood lined with sheet lead 0.12 inch thick, in which the zinc vitriol is allowed to crystallise out for 5 to 6 days.

The concentration of the solution from 30° to 50°B. takes about 20 hours, the consumption of coal being from 17 to 18 cwts. The cooling tanks are 32 feet 9 inches long, 5 feet broad, 16 inches deep at the sides, and 20 inches in the centre. The crystallised vitriol is dried. It has the following composition:—

	Per Cent.
ZnO . . . . .	25·45
MnO . . . . .	2·32
FeO . . . . .	0·47
SO <sub>3</sub> . . . . .	29·54
CuO . . . . .	trace
H <sub>2</sub> O . . . . .	41·67

The presence of manganese gives it a pale pink colour. The mother liquor is pumped back into the evaporating pans until it becomes too impure.

A portion of the zinc vitriol is worked up into calcined vitriol. For this purpose it is heated in copper or wrought-iron pans, 3 feet 3 inches deep and 4 feet in maximum diameter, until it melts in its water of crystallisation, when it is stirred continually for 3 or 4 hours. The impurities that separate out are then skimmed off, and it is finally ladled into wooden tanks, in which it is stirred with wooden paddles until it solidifies to a fine grained mass. It is then sifted and packed in barrels. At the Sophia Works 266 tons of crystallised vitriol produced 232 tons of calcined vitriol, with a consumption of 2,750 cubic feet of cord-wood.

*Treatment of Zinc Blende containing Barytes.*—Dorsewagen<sup>1</sup> bases on his experiments a method of treating such ores, which consists in mixing the finely divided ores with weak brine in revolving barrels, and chlorinating at a temperature of 30° to 40° C. Sulphur separates out and zinc chloride is formed; after leaching out the latter its solution is evaporated, the residual zinc chloride dehydrated, then mixed with oxides of metals and calcium carbide and smelted for zinc alloys.<sup>2</sup> There are no details of the working of this process.

<sup>1</sup> *Zeit. d. ver. deutsch. Ing.*, 1902, p. 163-4.

<sup>2</sup> Borchers, *op. cit.*, p. 395.



# CADMIUM

## PHYSICAL PROPERTIES

CADMIUM has a white colour with a bluish tinge; its structure is dense, its fracture hackly. It crystallises in the forms of the cubical system. It is soft and ductile, and can be both beaten out into thin foil and drawn into wire. It is intermediate between tin and gold in hardness and tenacity.

Its specific gravity when cast is said to be 8·604, when hammered 8·694.

When bent it "cries" like tin.

Its melting point is 316° C. according to Wood, 320° C. according to Rudberg, and 355° C. according to Wagner. Its boiling point is given as 720° C. by Becquerel, and as 860° C. by Deville and Troost. Its vapour is orange-yellow and burns in the air, forming brown cadmic oxide.

An addition of zinc renders cadmium brittle.

It has the property of lowering the melting points of certain of its alloys. Thus Rose's metal, composed of 2 parts of bismuth, 1 part tin and 1 part lead, melting at 93 $\frac{3}{4}$ ° C., has its melting point brought down to 75° C. by the addition of 8 to 10 per cent. of cadmium. An alloy containing 8 parts lead, 15 parts bismuth, 4 parts tin and 3 parts cadmium becomes pasty at 60° C. and quite fluid at 70° C.<sup>1</sup> Lichtenberg's metal, which consists of 28·6 per cent. of bismuth, 42·8 of lead and 28·6 of tin, has its melting point lowered from 91·6° to 75° C. by the addition of 8 to 10 per cent. of cadmium, and the same amount reduces the melting point of Newton's metal—50 per cent. of bismuth, 31·25 of lead and 18·75 of tin—from 94·5° to 75° C.

<sup>1</sup> Lipowitz, *Dingler*, vol. 158, p. 376.

The melting point of *Sicherloth*, a soft solder containing 37 parts of lead and 63 parts of tin, is lowered by 8 per cent. of cadmium to  $136^{\circ}\text{C}$ ., and by 25 per cent. to  $132^{\circ}\text{C}$ .<sup>1</sup> Another solder (*Schnellloth*) composed of 1 part of cadmium, 1 of lead and 2 of tin melts at  $149^{\circ}\text{C}$ . An alloy of cadmium and tin of the composition  $\text{CdSn}_2$ , which is very malleable, melts at  $173.8^{\circ}\text{C}$ . The melting points of some other alloys of cadmium are here given:—

Alloy containing Cd 25 per cent. Sn 50 per cent. Pb 25 per cent. melts at  $150^{\circ}\text{C}$ .

Alloy containing Cd 5.2 per cent. Sn 9.4 per cent. Pb 35.4 per cent. Bi 50 per cent. melts at  $76.6^{\circ}\text{C}$ .

Alloy containing Cd 5.0 per cent. Sn 15.0 per cent. Pb 25.0 per cent. Bi 55 per cent. melts at  $60^{\circ}\text{C}$ .

#### THE CHEMICAL PROPERTIES OF CADMIUM AND OF ITS COMPOUNDS THAT ARE OF IMPORTANCE IN ITS EXTRACTION

When heated in the air to its boiling point, cadmium burns to an amorphous brown oxide, infusible at a white heat. It only decomposes water when water vapour and cadmium vapour are allowed to interact at a red heat. At lower temperatures it only decomposes water in the presence of acids. It is soluble in hydrochloric, nitric and sulphuric acids. Zinc precipitates it from its solutions. Sulphuretted hydrogen precipitates it from moderately acid solutions as a sulphide of various shades of yellow. According to Niederländer,<sup>2</sup> cadmium sulphide of a pale yellow colour is produced from solution of the chloride or the sulphate when the current of sulphuretted hydrogen is interrupted after half the metal has been precipitated, when the gas is allowed to come into contact as little as possible with the precipitate, and when the latter is washed with hot water. The dark yellow sulphide is produced by complete precipitation with constant stirring and heating of the precipitate during the whole period of the operation. A 10 per cent. solution is best suited to the production of both the pale and dark yellow sulphide.

Orange-yellow cadmium sulphide is produced when sulphuretted hydrogen is passed into a nearly boiling 2 per cent. solution of the chloride containing 5 per cent. of free hydrochloric acid, the precipitate being constantly stirred throughout the precipitation.

Cadmium sulphide is not decomposed by the heat of the

<sup>1</sup> Hauer, *Dingler*, vol. 177, p. 154.

<sup>2</sup> *Chemiker Zeitung*, 1893, No. 82.

electric current.<sup>1</sup> Cadmium oxide is reduced to metal by carbon and carbon monoxide in the same way as zinc, the temperature of reduction being, however, lower than in the case of the latter metal. As cadmium also volatilises at a lower temperature than zinc, these metals can be separated in the dry way without any special difficulty.

Cadmium hydrate is soluble in ammonia, but insoluble in excess of the carbonates of potash, soda or ammonia.

Cadmium alloys with many of the heavy metals; its alloys with gold, platinum and copper alone are brittle, those with lead and tin ductile; its alloys with silver and mercury are ductile only in certain proportions. Alloys of silver, copper and cadmium which vary in composition between 980 parts of silver, 15 of copper, 5 of cadmium and 500 of silver, 30 of copper and 470 of cadmium, are very ductile, as are also alloys of the following composition:—

750 Au + 166 Ag + 84 Cd

750 Au + 125 Ag + 125 Cd

746 Au + 114 Ag + 43 Cd + 97 Cu.

Zinc is rendered brittle and finely granular by a considerable admixture of cadmium.

### SOURCES OF CADMIUM

Cadmium occurs in nature as sulphide, CdS, with 77·6 per cent. cadmium, the mineral being known as Greenockite. It occurs at Przibram in Bohemia and at Neu-Sirka in the Siebenbürgen but in such small quantities (the Prehnite is an amygdaloid at Bishoptown in Scotland), that it cannot be regarded as a source of cadmium. The metallurgical sources of cadmium are the volatile bye-products obtained in smelting cadmium-bearing zinc ores. It occurs in small quantity in most zinc ores, especially in blende and calamine.

According to the researches of Jensch<sup>2</sup> the Upper Silesian zinc ores never contain more than 0·3 per cent. of cadmium. Higher contents than this given in the literature on the subject, appear only to refer to ores from the upper deposits. The percentage amounts

<sup>1</sup> Mourlot, *Compt. rendus*, 1897, 124, I., 768.

<sup>2</sup> *Sammlung chem. und chemisch-techn. Vorträge*, von Dr. Felix B. Ahrens, vol.

of cadmium in materials from various sources, as determined over a period of 10 years by Jensch, are here given:—

Coarse grains of blende from the Samuelsglück mine, Beuthen 0.095 (mean), blende slimes from the same place 0.01; blende coarse concentrates from Grosserschacht, Birkenhain 0.123, from the new Victoria mine, Karf, 0.068, blende from the jigging machines 0.23; blende slimes from the new Helene mine, Scharley 0.124 to 0.150, blende concentrates 0.160, lump calamine 0.186; blende concentrates from the Aufschluss mine, Beuthen 0.153, from the Newhof mine 0.172; blende from Maria mine, Miechowitz 0.232; lump calamine from Kramersglück mine, Beuthen 0.306, from the Karl Gustav mine, Tarnowitz 0.028, from the Medardus mine, Stollarzowitz 0.090; mixed calamine and blende from the Samuelsglück mine 0.194; slimes from the new Helene mine 0.006; calamine from the Karolinewunsch mine 0.009. The mean content of cadmium in the Upper Silesian ores is given by Jensch as 0.102 per cent.

Klieeisen found that the zinc blendes from the Upper Harz, which are stated in the literature to be rich in cadmium, contain at most 0.01 per cent. of cadmium; a whole series of grades of blende was found to be free from cadmium. The percentage of cadmium in blende from the Hercules mine, Schwarzenberg, Saxony, was found to be on the average 0.1, from Fürstenbrunn, Schwarzenberg, 0.065, from Carolinenthal, near the same place, 0.011, and from Breitenbrunn, Johann-Georgenstadt, 0.02. A sample of blende from Ueckerath, in Rhineland, gave 0.39, and the radiating blende from Przibram is said to have yielded up to 1.136. Belgian blendes are said to have given 0.13 to 0.21, and those from Sterzing, Tyrol, and from Stollersbachthal, Salzburg, over 0.2 per cent.

Zinc ores from Styria, Carinthia and Carniola contain but little cadmium, *e.g.*, blende from Cilli contained 0.005, from Feistritz on Drau 0.065; calamine from Feistritz 0.055 to 0.140, blende from Peggau 0.008, from Raibl 0.07, from Tarvis 0.022, from Feistritz-Paternion 0.008, from Rübland 0.02 to 0.036, and from Nötsch 0.009 to 0.015.

Blende from the Hungarian Erzgebirge gave, according to Jensch, traces to 0.009 per cent. of cadmium; honey-yellow blende from Felsöbanya 0.01; blende from Kapnik and Offenbanya, Hungary and from Rodna, Siebenbürgen, over 0.3. Black zinc blende from Finland contained 0.46 (Jensch), blende from Wanlockhead, Scotland, and from Matlock, Derbyshire, over 0.4.

Blendes from the Cantabrian coast, especially the transparent varieties from Cumillas, Santander, contain over 0.4 per cent.; Spanish

calamines are said to have been found with 2 to 5 per cent. The percentages in the Swedish blends are:—from the Borwall mine, Bolände, 0·17 to 0·40, from Schisshyttan 0·17 to 0·31, from Falun 0·17 to 0·36, from Korsnäs 0·22 to 0·35, from Oerebro, 0·18 to 0·37; ores exported from Gefle to Upper Silesia 0·11 to 0·22, from the Langfulla mine, Sunnansjö 0·075 to 0·082, from Nora 0·065, from Klippan 0·08, and from Mariedam 0·047 to 0·056.

Blende from Lapland contained 0·008, and from Faaberg, Lillehammer, in Norway, 0·01 per cent.

Cadmium has also been found in coal, being probably contained in the pyrites. Unwashed coal from Schmiederschacht, Poremba, in Upper Silesia, contained 0·008 per cent. of CdO, washed coal 0·001, coal dust from the Paulus mine, Morgenroth, 0·004, and coal dust from the Wolfgang mine, Ruda, 0·005 of cadmium oxide.

When zinc blende is roasted, a great part of its cadmium content is lost by volatilisation. Thus a blende from Upper Silesia contained 0·110 per cent. of cadmium before roasting and 0·042 after. For this reason the flue dust from the roasting furnaces always contains cadmium, the quantity varying from 0·22 to 2·02 per cent. (Jensch). Of the cadmium in the flue dust, 40 per cent. is in the form of sulphate. The mud obtained in neutralising the sulphur dioxide of the waste gases from the calcining furnaces by lime contains ordinarily 0·1 to 0·2 per cent. of cadmium. In smelting calcined calamine or roasted zinc ores, the cadmium becomes concentrated in the first volatile products, the zinc fume or dust; and these bodies, which may contain up to 30 per cent. of cadmium (as in the Belgian *poussière*), form the raw material for the production of cadmium. Zinc itself often contains cadmium.

Cadmium is used for the production of easily fusible alloys, of amalgam used for stopping teeth, of cadmium sulphide which serves as a yellow oil colour, of cadmium iodide and bromide for photography, of chloride for use in dyeing and cotton printing, and of the sulphate for medicinal purposes. On account of its limited applications, and of its low price due thereto, only small quantities of cadmium are ever extracted.

### THE EXTRACTION OF CADMIUM

Cadmium may be obtained by both dry and wet methods; no attempts have yet been made to produce it electrolytically.

It is, as a rule, obtained at present in the dry way. The methods that have been proposed for its wet extraction have not as yet been put into practice.

*Extraction in the Dry Way*

The extraction of cadmium in the dry way depends upon the property of cadmium oxide of being reducible to metallic cadmium vapour by the action of carbon and carbon monoxide, at a temperature below that at which zinc oxide is reducible to metal, and upon the property of metallic cadmium of volatilising at a lower temperature than metallic zinc.

If a mixture of zinc and cadmium oxide is accordingly exposed to the action of carbon in retorts at a comparatively low temperature, about redness, cadmium is reduced first and vaporised, and can therefore be condensed in receivers and thus separated from the zinc. When a mixture of zinc oxide, zinc, cadmium oxide, and cadmium, with a comparatively low percentage of cadmium, such as forms the usual material for the extraction of cadmium, is reduced by carbon, a pulverulent mass is obtained in the receiver, consisting of cadmium oxide, cadmium, zinc oxide, and zinc, considerably richer in cadmium than was the original mixture. Cadmium can be extracted from this mixture either direct or after another further enrichment by a repetition of the process of distillation.

The raw material is, as already stated, obtained in the process of zinc distillation, the easily reducible and volatile cadmium mixed with zinc dust and zinc oxide being deposited in the cones attached to the adapters for the zinc distillation, or in the first dust chambers connected with these.

The largest cadmium works in the world are in Upper Silesia, where the material used is either the *first poussière*, that is to say the flue-dust or zinc dust collected during the first  $1\frac{1}{2}$  or 2 hours of the distillation in the sheet-iron cones attached to the adapters, and which contains up to 6 (less frequently up to 8) per cent. of cadmium, or the zinc dust deposited in the first portion of the dust chambers which form the continuation of the Kleeman and Dagner adapters. This dust contains 1.2 to 3 per cent. of cadmium. It is mixed with a suitable proportion of coal, and is distilled at a low red heat in the retorts that are used for zinc extraction, long sheet-iron cones being used as adapters; cadmium collects in the latter, intermixed with cadmium oxide, zinc, and zinc oxide. The material so enriched is mixed with charcoal and distilled in small cast-iron or clay retorts; the former, used at Lipine, are furnished with long conical sheet-iron adapters. The latter have no adapters, but are set at an angle, so that the cadmium collects in the front portion, whence it can be drawn off through a tap-hole and cast into moulds. Cadmium

collects in the adapters of the cast-iron retorts in the solid state. It is transferred to a ladle, covered with a layer of the oxides cleaned out from the retorts, then with a layer of tallow, and melted. After fusion it is allowed to cool down somewhat, and is then cast in moulds made of paper rolled up so as to produce rods weighing 2 to 3 ounces each. The cadmium collected in the clay retorts is tapped out into ladles and poured direct into cast-iron moulds made in halves, which also produce it in the form of rods.

The loss of cadmium in these operations is very great, owing to volatility, absorption of oxide by the muffle walls, and retention in the residues. It amounts to 65 to 70 per cent., inclusive of the cadmium in the residues. The first two causes of loss also, along with the absorption of cadmium by the adapters, are operative during the distillation of the zinc ores, and account for the disappearance of much of the cadmium content of the ores. Thus Jensch<sup>1</sup> found 0.052 per cent. of cadmium in muffle fragments and 0.13 per cent. in adapter fragments. These are, however, treated again along with the zinc ores. The dust which collects on the ironwork of the furnace was found to contain 0.7 per cent. of cadmium.

At Lipine the dust-catcher connected with the Kleeman adapters, in which latter a good deal of cadmium is volatilised, yields flue-dust containing at the outside 3 per cent. of cadmium. Dust containing 5 to 6 per cent. of cadmium may be obtained by using globular sheet-iron receivers attached to the adapters; these are taken off at the expiration of 1½ to 2 hours, and the dust that clings to the sides is shaken out.

The flue-dust so obtained is next treated in an ordinary zinc muffle provided with a taper conical sheet-iron adapter about 3 feet long. The charge for the muffle consists of 55 lb. of flue-dust and 44 lb. of *cinder*. Distillation takes about 22 hours, and the working about 2 hours. Flue-dust is deposited on the inside of the adapter, considerably enriched in cadmium, but containing widely varying amounts of that metal. It is further treated in cast-iron retorts, 2 inches high in the clear and 6.7 inches wide, the metal being about 1 inch thick; these are provided with a tapering conical sheet-iron adapter, about 16 inches in length. Cadmium in the form of drops and cadmium oxide are deposited inside the adapter; this mixture is transferred to a small cast-iron ladle and heated under a layer of tallow, the molten cadmium being then cast into rods. The residues from the muffles and retorts are returned to a subsequent charge.

<sup>1</sup> *Op. cit.*, p. 213.

At the Paul Works, in Upper Silesia, flue-dust collected from the flues connected with the Dagner adapter is used as a source of cadmium. It contains 3 to 4 per cent. of cadmium, and is distilled, as at Lipine, at a red heat for 24 hours in ordinary zinc muffles provided with a conical sheet-iron adapter. Flue-dust with 20 per cent. of cadmium is thus obtained, which is mixed with *cinder* and distilled in a cylindrical clay retort about 10 inches in diameter and 4 feet long, the operation lasting 24 hours. The charge for a retort is 33 lb. The retort has no adapter, and inclines towards the front of the furnace; the cadmium collects in this portion of the retort, and is tapped through a small hole into a ladle from which it is poured direct into moulds. The residues from the retorts are added to the charges for zinc distillation.

At the Wilhelmina Works zinc dust containing 3 to 4 per cent. of cadmium is distilled from muffles 6 feet long, the charge consisting

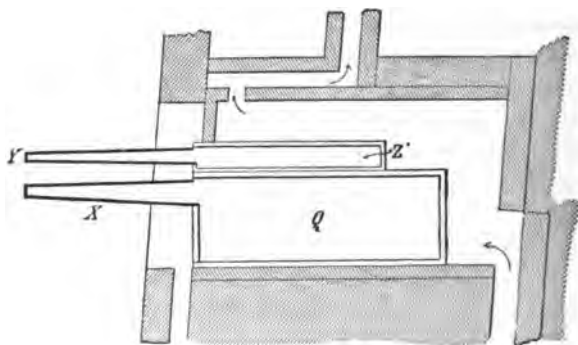


FIG. 263.

of 250 lb. of zinc dust and 38 lb. of coke, and the distillation lasts 22 hours. The metal is separated from the oxide which collects in the adapter, melted and cast into sticks, and the dust is gathered together and distilled every 3 days in smaller retorts, yielding thereby cadmium with only 0.5 per cent. of foreign bodies. This also is re-melted and cast into sticks. The distillation residues are added to the charges for zinc distillation. The arrangement of a furnace holding both a large and a small retort is shown in Fig. 263, where *Q* is the large, *Z'* the small retort, *X* the adapter of the larger retort, and *Y* that of the smaller.

From zinc dust at the Kunigund Works containing 3.88 to 4.5 per cent. of cadmium, Jensch<sup>1</sup> obtained on the first distillation an

<sup>1</sup> *Ibid.*



enriched dust averaging 52·2 per cent., and this on further distillation gave dust containing 94·2 to 99·89 per cent. of cadmium. The yield of cadmium from the first dust was estimated at 31·26 per cent., the large loss being attributed to the causes mentioned above.

At Engis, in Belgium,<sup>1</sup> zinc dust averaging 1·5 to 1·6 per cent. of cadmium is mixed with coal dust and treated in Belgian furnaces carrying three rows of small cast iron tubes with cast-iron adapters and sheet-iron nozzles, the product being dust with 6 per cent. of cadmium. In 12 hours 2 cwt. of dust is treated in 11 tubes, yielding 28 to 32 lb. of enriched dust. The latter is distilled again in the same plant, producing metallic cadmium, 28 to 32 lb. being treated in 12 hours in four tubes. The cadmium collects in the adapters, whence it is drawn off at intervals of 1 hour, so that it shall be as free from zinc and iron as possible. It is then cast into moulds. The residues from the distillation contain 0·30 per cent. of cadmium; of the cadmium contents of the original dust, 30·12 per cent. is saved, 21·17 per cent. is left in the residues and 48·71 per cent. is volatilised. Three grades of cadmium are produced; the purest kind, which is readily bent, amounts to about one-half of the total; the next contains 75 per cent. of cadmium and can be bent with difficulty but yet without breaking, whilst the poorest quality contains only 40 per cent. of cadmium and is very brittle. Grades containing less than 99·5 per cent. of cadmium are at present unsaleable, and must be purified by fractional distillation. According to R. Wagner, a sample of Silesian cadmium had the following composition:—

Cd . . . . .	94·86
Zn . . . . .	4·96
Fe . . . . .	0·23
Sp. gr. 8·528	Melting point 368° C.

Cadmium from the Kunigund Works gave in analysis <sup>2</sup>

Cd . . . . .	99·80
Fe . . . . .	0·005

and another sample from Upper Silesia,

Cd . . . . .	99·65
Fe . . . . .	0·01

Thallium was found in some samples of cadmium by Crookes.

<sup>1</sup> Städler, *Journ. f. Pract. Chem.*, 1864, vol. 91, p. 359; *Dingler*, vol. 173, p. 286.

<sup>2</sup> Jensch, *op. cit.*, p. 220.

*Extraction of Cadmium in the Wet Way*

Wet processes have been proposed for extracting cadmium both from zinc fume and from metallic zinc containing cadmium,<sup>1</sup> but have not yet come into use.

The older suggestions depend upon the fact that when the above substances are treated with hydrochloric acid, zinc dissolves before cadmium, whilst the latter metal can be thrown down from its solutions by the former. The substances are to be treated with hydrochloric acid in such quantity that a portion of the zinc remains undissolved and can thus precipitate any cadmium that may have gone into solution; any lead present will also be found in the residue; even if dissolved it is precipitated by the zinc. The latter is then treated with hydrochloric acid until a little cadmium has gone into solution, thus showing that all the zinc has been dissolved out. The cadmium is thrown down from the solution by means of rods of zinc. The mixture of lead and cadmium is then subjected to distillation. The solution is to be neutralised with zinc fume, and the zinc thrown down from it as a hydrate by milk of lime.

Another method for obtaining cadmium sulphide or oxide has been proposed by Kosmann<sup>2</sup> for the flue-dust of the zinc reduction and blend calcination furnaces in Upper Silesia.

The flue-dust from the zinc furnaces, the composition of which has been given on page 216, is to be treated with neutral ammonium carbonate, which dissolves the zinc, whilst the cadmium remains as insoluble carbonate. The solution is heated, when ammonia and a part of the carbon dioxide are driven off, whilst basic zinc carbonate is formed which can be converted into zinc oxide by heating. The residue is heated to convert the carbonate of lead present into oxide, and is then digested with solution of lead acetate, which dissolves the oxide of lead. Carbon dioxide is passed into the solution, precipitating the lead as white lead. The residue that is left, containing the cadmium, either as oxide or as carbonate, may be treated with dilute sulphuric acid to dissolve the cadmium, which may be thrown down as sulphide by means of sulphuretted hydrogen. If cadmium oxide is to be produced, the residue is treated with nitric acid, the solution of cadmium nitrate is evaporated and the salt heated, when brown cadmium oxide is left behind.

This process has never come into use.

Flue-dust obtained in calcining blende from Upper Silesia also

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1862, p. 305.

<sup>2</sup> *Preuss. Minist. Zeitschr.*, 1883, p. 238.

contains cadmium; it is partly soluble and partly insoluble in water. The composition of two samples from the Silesia and Godulla works respectively is shown by the subjoined analyses<sup>1</sup>:—

I. FLUE-DUST FROM THE SILESIA WORKS.

	Soluble.	Insoluble.	Insoluble per cent.
ZnO . . . . .	17·144	7·192	16·809
PbO . . . . .	—	6·285	14·690
CdO . . . . .	0·874	1·147	2·680
TiO . . . . .	0·006	—	—
FeO . . . . .	1·896	—	—
MnO . . . . .	1·332	0·042(Mn <sub>2</sub> O <sub>3</sub> )	0·098
Fe <sub>2</sub> O <sub>3</sub> . . . . .	} 2·900	9·043	21·135
Al <sub>2</sub> O <sub>3</sub> . . . . .		3·115	7·280
CaO . . . . .		0·478	1·117
MgO . . . . .	0·168	0·440	1·028
As <sub>2</sub> O <sub>3</sub> . . . . .	—	0·401	0·937
P <sub>2</sub> O <sub>5</sub> . . . . .	—	0·263	0·614
SO <sub>2</sub> . . . . .	20·430	6·612	15·453
H <sub>2</sub> O . . . . .	11·400	—	—
Residue . . . . .	—	7·765	18·146
	56·864	42·786	99·997
	99·650		

II. FLUE-DUST FROM THE GODULLA WORKS.

	Soluble.	Insoluble.	Insoluble per cent.
ZnO . . . . .	10·991	9·532	15·430
PbO . . . . .	—	8·980	14·486
CdO . . . . .	1·120	1·518	2·449
TiO . . . . .	0·006	—	—
FeO . . . . .	1·676	—	—
MnO . . . . .	0·481	1·591(Mn <sub>2</sub> O <sub>3</sub> )	2·566
Fe <sub>2</sub> O <sub>3</sub> . . . . .	2·940	15·928	25·696
Al <sub>2</sub> O <sub>3</sub> . . . . .	1·191	4·601	7·423
CaO . . . . .	0·464	1·071	1·640
MgO . . . . .	1·337	0·858	1·065
As <sub>2</sub> O <sub>3</sub> . . . . .	—	1·280	2·066
P <sub>2</sub> O <sub>5</sub> . . . . .	—	0·394	0·604
SO <sub>2</sub> . . . . .	13·320	9·061	15·101
H <sub>2</sub> O . . . . .	4·850	—	—
Residue . . . . .	—	6·804	10·976
	38·376	61·618	99·502
	99·994		

Kosmann proposes to treat this flue-dust first with water and then with sulphuric acid: the cadmium is dissolved as sulphate, in

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1862, p 505.

part in the aqueous solution, in part by the acid. The solutions are mixed and heated, to precipitate iron and calcium sulphate. The solution is then diluted with water, and the cadmium precipitated as sulphide. Arsenic is precipitated as sulphide along with it, and is said to improve its colour. If cadmium oxide is required, the sulphide is to be roasted, the arsenic being volatilised as trioxide and condensed.

This process also has not come into use. In experiments to obtain cadmium in the wet way from the dust, great care must be taken owing to the amount of arsenic present.

### *Extraction of Cadmium by Electrolytic Methods*

Borchers<sup>1</sup> was able to precipitate compact cadmium from its solutions in laboratory experiments, using a current of 6 to 14 ampères per square foot; it may therefore be obtained in form fit for use more readily than zinc.

Brand<sup>2</sup> also obtained favourable results in experiments on the purification of cadmium contaminated with zinc and other metals by electrolytic methods; the tension in the bath was low, and the metal obtained quite pure. He used for his anodes plates of impure cast cadmium, containing cadmium 88·7 per cent., zinc 8·55 per cent., lead 1·45 per cent., copper 1·35 per cent., with smaller amounts of antimony, arsenic, bismuth, and iron; his electrolyte was a solution of cadmium sulphate with 5 per cent. of free sulphuric acid and 0·8 lb. cadmium to the gallon. With electrodes 2 inches apart, and a current intensity of 12·8 ampères, the tension in the bath was only 0·042 volt, because the solution of the zinc, which remained in the electrolyte, introduced a considerable amount of electric energy into the circuit. The tension increased to 0·048 volt as soon as the solution contained, together with 5 per cent. of sulphuric acid, 0·464 lb. of zinc and 0·04 lb. of cadmium to the gallon.

Mylius and Fromm<sup>3</sup> obtained cadmium in compact form by the use of current densities of 4·6 to 9·25 ampères per square foot.

<sup>1</sup> *Elektro-metallurgie*, 1895, p. 298, 1903, p. 451.

<sup>2</sup> *Dammer, Chem. Technol.*, vol. ii., pp. 33, 687.

<sup>3</sup> *Zeits. für anorg. Chemie.*, 1898, 13, 157.

## MERCURY

### PHYSICAL PROPERTIES

MERCURY or quicksilver is the only metal fluid at ordinary temperatures; it has a silver-white colour with a slight bluish tinge, and a perfect metallic lustre. According to Melsens, it is transparent in thin layers, showing a blue colour with a somewhat violet tinge. According to Cavendish, it solidifies at  $-39.38^{\circ}$  C.; according to Hutchins, at  $-39.44^{\circ}$  C., and according to Mallet, at  $-38.85^{\circ}$  C. It contracts upon solidification, and forms a white, very ductile and malleable mass, which is readily cut with a knife. It raises blisters on the human skin on contact, just like red-hot metal. Its specific gravity, when fluid, at  $0^{\circ}$  C., is 13.5959 according to Regnault, 13.595 according to Kopp, and 13.589 according to Biot and Arago. The specific gravity of solid mercury is 14.1932. It crystallises in the forms of the cubical system. The specific heat of solid mercury between  $-78^{\circ}$  and  $-40^{\circ}$  C. is 0.0247, that of the fluid metal, between  $0^{\circ}$  and  $100^{\circ}$  C., is 0.0333. Its electrical conductivity according to Matthiesen at  $22.8^{\circ}$  C. is 1.63, silver at  $0^{\circ}$  being taken as 100. Its thermal conductivity according to Calvert and Johnson is 677, compared to that of silver taken as 1,000. Mercury is volatile to a slight extent at ordinary temperatures, and according to Merget even below  $-44^{\circ}$  C. This may be proved by suspending gold leaf above a vessel containing mercury, when it will become coated at ordinary temperatures with a white layer of amalgam. The boiling point of mercury, according to Dulong and Petit, is  $360^{\circ}$  according to Regnault,  $357.25^{\circ}$  C.; it is converted into a colourless vapour, the density of which is given as between 6.7 and 7.03. The rapidity with which mercury volatilises on boiling depends to a great extent upon its purity. It is mainly diminished by lead and zinc, and on the contrary increased by platinum. Millon showed that in the same time and under otherwise similar conditions, thirteen times as much pure mercury was volatilised as a mercury containing 15.166 of lead. Platinum increases the rapidity of evaporation if

digested for one or two days with mercury at a temperature of  $50^{\circ}$  to  $80^{\circ}$  C. Iridium, gold, silver, copper, nickel, cadmium, and arsenic have no influence upon the rapidity of evaporation.

At the ordinary temperature the cohesion of pure mercury considerably surpasses its adhesion to lighter bodies. When, therefore, it is allowed to run over an inclined surface of paper or glass, it forms spherical masses or globules. When it is impure, it leaves a film upon the above-named surfaces, and does not run in spherical globules but in pear-shaped ones. When agitated with air, it leaves a black powder; by violent agitation of mercury with various fluids, as also by rubbing it up with certain bodies such as sugar and grease, it is converted into a fine dark gray powder. Vapours of mercury have a most injurious effect upon the animal system. In all operations in which mercury vapours are evolved, it is, therefore, necessary to take especial precautions to protect the persons engaged therein.

#### CHEMICAL PROPERTIES OF MERCURY AND OF ITS COMPOUNDS, WHICH ARE OF IMPORTANCE FOR THE EXTRACTION OF THE METAL

Pure mercury is unchanged in dry air at the ordinary temperature; neither is it affected by long-continued agitation with air, oxygen, nitrous oxide, nitric oxide, or carbon dioxide. In damp air, however, it gradually becomes coated with a thin film of mercurous oxide ( $\text{Hg}_2\text{O}$ ). Impure mercury becomes coated with a film of oxide even in dry air. If mercury is heated for a considerable time up to  $350^{\circ}$  C. in the air, it oxidises to mercuric oxide ( $\text{HgO}$ ), which, according to Pelouze, is crystalline. This gradually decomposes in the sunlight into mercury and oxygen. When heated it is rapidly decomposed, the mercury being volatilised. When again cooled down, it is partly reconverted into mercuric oxide. Mercury distilled by heating the latter, is, therefore, rendered impure by oxide and is accordingly somewhat pasty.

Mercuric oxide produced in the wet way by precipitation from mercuric salts has a bright orange-yellow colour, which, according to Pelouze, is an amorphous modification of mercuric oxide.

Dilute sulphuric acid has no action upon mercury. Concentrated boiling sulphuric acid dissolves it with the evolution of sulphur dioxide. When mercury in excess is present, the mercurous salt is produced; with excess of sulphuric acid, on the other hand, the mercuric salt is formed. Hydrochloric acid does not attack mercury. Nitric acid, even when dilute, dissolves mercury, forming a nitrate

the mercurous salt being formed in the presence of an excess of mercury and when cold acid is employed, but the mercuric salt when heated with an excess of acid or when strong acid is used.

Mercurous salts, as also mercuric sulphate and nitrate, are decomposed by water into soluble acid and insoluble basic salts. Mercurous salts when heated decompose, producing mercuric salts and metallic mercury.

Aqua regia dissolves mercury with comparative readiness, mercuric chloride ( $\text{HgCl}_2$ ) being formed. Chlorine in the gaseous condition or in solution in water attacks mercury at ordinary temperatures, mercurous chloride being formed, and gray pulverulent mercury being produced. Boiling mercury burns in chlorine gas with a yellowish-red flame, forming mercurous and mercuric chlorides.

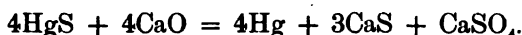
Mercuric chloride, so-called corrosive sublimate, is prepared by dissolving mercury in aqua regia, by dissolving mercuric oxide in hydrochloric acid, or by the addition of common salt to mercuric sulphate. Mercurous chloride, known as calomel, is produced by treating mercuric chloride with mercury or by precipitating mercurous salts by means of hydrochloric acid. Both chlorides have a white colour and are volatilised on heating, mercurous chloride subliming without previous fusion. Mercuric chloride is readily soluble in water; mercurous chloride is soluble neither in water nor in dilute acids.

Sulphide of mercury ( $\text{HgS}$ ), the most important compound of mercury for the metallurgist, occurring native as cinnabar, can be produced as an amorphous black mass by rubbing together flowers of sulphur and mercury and by gently heating the nixture of the two bodies. If this mass is heated to its melting point, mercuric sulphide volatilises, and may be condensed in the form of a brownish red crystalline sublimate. This on grinding becomes scarlet and forms artificial cinnabar. When gently heated, air being excluded, it is readily reconverted into black amorphous mercuric sulphide, but if heated more strongly, it again sublimes as red sulphide. Native cinnabar begins to darken at  $200^\circ \text{C}$ ., and to volatilise; at  $350^\circ$  it volatilises to a very great extent, but for its complete volatilisation a low red heat,  $500^\circ$  to  $600^\circ \text{C}$ ., is required. With excess of air, it burns at  $350^\circ \text{C}$ . with a blue flame of sulphur, forming sulphur dioxide, metallic mercury separating out and volatilising. The red sulphide of mercury darkens under the action of light, and after a considerable time it becomes black

in consequence of the separation of free mercury. The specific gravity of artificial cinnabar is 8.124, according to Boullay, whilst the specific gravity of its vapour, according to Mitscherlich, is 5.51. It is, therefore, assumed that upon the volatilisation of sulphide of mercury, partial dissociation takes place. Mercuric sulphide can be produced in the wet way by the action of alkaline polysulphides upon mercury, or by the action of sulphuretted hydrogen or alkaline sulphides upon solutions of mercuric salts. In these processes black mercuric sulphide is obtained. If the latter is brought into contact with alkaline polysulphides it passes into red mercuric sulphide slowly in the cold, but rapidly on heating. This phenomenon, which has been utilised for the production of artificial cinnabar in the wet way, has been explained by supposing that black mercuric sulphide dissolves in solutions of alkaline polysulphides, and crystallises out of the solution in the form of the red sulphide. Mercuric sulphide is not attacked by hot nitric acid. Aqua regia dissolves it rapidly with the formation of sulphuric acid and the separation of sulphur. Mercuric sulphide forms double sulphides with the sulphides of the alkalis. The potassium salt, for instance, has the formula  $\text{HgS}, \text{K}_2\text{S} + x\text{H}_2\text{O}$ ; it contains variable quantities of water according to the temperature and the concentration of the solution. A portion of these double sulphides is soluble in water in the presence of caustic alkalis, but at a certain degree of dilution is decomposed again into its constituents. Mercuric sulphide forms peculiar double compounds with mercury and copper salts. For instance, by passing sulphuretted hydrogen into a solution of mercuric chloride, a white deposit of the composition  $2\text{HgS} + \text{HgCl}_2$  is first formed, which becomes yellow and finally black under the continued action of sulphuretted hydrogen. Sulphide of mercury is soluble in solutions of sodio-cuprous chloride. Mercuric sulphide is soluble in bromine. According to Regnault, mercuric sulphide is partly decomposed by water vapour, sulphuretted hydrogen being formed and mercury separating out together with a black sublimate. When sulphide of mercury is heated with carbon it is partly decomposed, according to Berthier, carbon bisulphide being formed, and mercury separating out. When heated with other metals which possess a greater affinity for sulphur than mercury, for example with iron, tin, or antimony, the mercury is liberated in the form of vapour, whilst the sulphur combines with the respective metals. Copper and zinc are said by Heumann to decompose cinnabar at the boiling point of water, or at ordinary temperatures under pressure. When mercuric sulphide is heated with lime the



mercury separates out and volatilises, sulphide and sulphate of calcium being produced, as shown by the following equation :—



### *Alloys of Mercury*

Mercury combines directly with most metals in all proportions, forming amalgams; with gold, silver, zinc, tin, cadmium, lead, and bismuth it amalgamates readily; copper amalgamates easily when finely divided, but with difficulty in the massive state; arsenic, antimony, and platinum amalgamate with difficulty, iron, nickel, and cobalt not at all directly. The amalgams of the last named three metals can only be produced indirectly under certain conditions, for example, by means of electrolysis when a solution of a mercuric salt is used for the electrolyte and one of the above named metals as cathode, or when sodium amalgam is brought in contact with solutions of these metals, or when the metals are brought in contact with solutions of mercury. These amalgams are very unstable, and decompose readily, iron amalgam, for instance, when violently agitated. When mercury amalgams are heated to the boiling point of mercury, the latter separates in the form of vapour, whilst the respective metals are set free.

### ORES OF MERCURY

Mercury occurs in nature in but relatively few minerals. The only ore of mercury which occurs in considerable quantities in nature, and which alone forms the object of an independent extraction of mercury, is cinnabar. Native mercury often occurs with this ore, but only in very subordinate quantities. The other true ores of mercury are of no importance for the extraction of that metal. In addition to the true ores of mercury, mercury occurs isomorphously intermixed with other minerals, especially with fahlores, and in very minute quantities in zinc blendes. In the fahlores, in some localities, it is contained in such quantity that these are worth treating for mercury.

### *Native Mercury*

This generally occurs in deposits of cinnabar as a decomposition product of that mineral, and, therefore, generally near the outcrop of such deposits. In these it is generally found in the form of small disseminated globules or in filiform masses. It is rare to find

the individual globules so large that the mercury can be collected from them. Considerable quantities of native mercury disseminated through serpentine have been found, for instance, at the outcrops of various deposits of cinnabar in California (Sonoma Mine, Rattlesnake Mine, Wall Street Mine). It is said to occur in a decomposed granite, unaccompanied by cinnabar, in the neighbourhood of Limoges, especially at Mélinot near St. Lô, and also, accompanied by calomel, in the strata upon which the town of Montpellier stands. It occurs alloyed with silver in the form of *native amalgam*, which contains 26.5 to 35 per cent. of mercury, and is looked upon as a silver ore. This mineral has been found at Moschellandsberg in the Rhine Provinces, at Rosenau in Hungary, Allemant in France, and Argueros in the province of Coquimbo in Chili.

#### *Cinnabar or Cinnabarite (HgS)*

This mineral contains 86.2 per cent. of mercury, and is the only ore which is regularly worked for mercury, on which account it deserves fuller consideration. It but rarely occurs in large masses, but generally disseminated or intermixed with metallic oxides, earths, bituminous substances, or iron pyrites; of the metallic minerals, iron pyrites is the most frequent, followed by arsenical and antimonial compounds, and ores of gold, copper, and zinc. As regards its geological distribution, it may be noticed that it occurs in strata of almost all ages from Archaean crystalline schists to Quaternary deposits. It is also found in deposits from eruptive rocks and from sulphurous springs of volcanic origin, as also at times in the eruptive rocks themselves. It is still being deposited in the fumaroles of Sulphur Bank, near Clear Lake, in California.

Cinnabar is dimorphous. In addition to the red crystalline variety, there is also a black variety possessing no crystalline structure and having a lower specific gravity than red cinnabar, which is known as meta-cinnabarite. Cinnabar intermixed with bituminous bodies, which give it a dark red to black colour, is known as hepatic cinnabar. Idrialite is a mixture of cinnabar with idrialine ( $C_8H_2$ ), occurring at Idria. Coralline ore is a mixture of cinnabar, bituminous matters, and about 60 per cent. of calcium phosphate.

Cinnabar occurs at relatively few places in the world in sufficient quantity to be worked for the extraction of mercury. In Europe the most important localities which furnish the largest quantities of mercury are Almaden, in Spain; Idria, in Carniola; and Nikitowka, in the South of Russia.

At Almaden, on the northern slopes of the Sierra Morena between Badajoz and Ciudad Real, cinnabar occurs together with native mercury in an area 10 miles long and 6 miles broad, in Silurian and Devonian strata, consisting of slates, quartzites, sandstones, and small quantities of limestone, forming three almost vertical tabular deposits about 600 feet in length and 12 to 25 feet wide. In these deposits it occurs both in masses and disseminated. The content of mercury of the different grades of ores vary from 0·75 up to 25·05 per cent.; it is said to average 8 to 9 per cent. These deposits were known to Theophrastus, as early as 300 B.C., and they are still to-day the most important mercury deposits in Europe.

At Idria, in Austria-Hungary, cinnabar, hepatic ore, and coralline ore occur with native mercury in irregular deposits in Triassic strata. The deposits are partly of the nature of a stockwork, partly contact veins between limestone and dolomite, the various grades of ore containing from 0·2 to 30 per cent. of mercury, the average of the ores being from 0·5 to 0·8 per cent. This deposit was known in the year 1490, and is, after Almaden, the most important in Europe.

At Nikitowka, a station on the Kursk-Charkoff-Azov railway line, in the district of Bachmut of the government of Ekaterinoslav in the South of Russia, cinnabar occurs impregnating sandstone strata of carboniferous age, having a thickness of 46 feet. The average proportion of mercury contained in this important deposit is given as 0·6 per cent. As is shown by old exhausted spoil heaps, this deposit has been worked in ancient and as yet undetermined times. Operations were recommenced only in the year 1886, and at present ores are produced in such quantities that the mercury produced at the works attached to the mine not only supplies the demands of Russia, but is exported in considerable quantities. It may be considered as one of the most important deposits of the whole world. Regarded as a single works, it is the most important in Europe after Almaden and Idria. At Vallalta, near Agorda, in the north-west of the state of Venice, cinnabar occurs in the form of impregnations, but the ores are relatively poor. At Monte Amiata, in Tuscany, cinnabar occurs in Eocene formations at Siele, Solforate, Montebuono, Pian Castagnio, Abbadia San Salvatore, and in the Lias at Cornacchino.<sup>1</sup> The deposits are considerable, the output of mercury at Monte Amiata being the fourth greatest in Europe. The ores are smelted at Siele,

<sup>1</sup> Th. Haupt, *Berg- und Hüttenm. Ztg.*, 1884; P. de Ferrari, *Die Quicksilverminen des Monte Amiata*, Florence, 1890; R. Rosenlecher, *Zeits. für praktische Geologie*, 1894, p. 337; N. Novarese, *Ibid.*, 1895, p. 60; V. Spirek, *Das Zinnobererzvorkommen im Monte Amiata*, *Zeits. für praktische Geologie*, 1897, p. 369.

Cornacchino, Montebuono, and Abbadia San Salvador in Spirek furnaces. The average content of quicksilver in the ores treated is 0.4 per cent. at Montebuono and 1.2 per cent. at Siele. A recently discovered (1883) deposit of cinnabar of a certain importance is that in the Avala Hills, near Belgrade, in Servia, where mercury is also extracted. Cinnabar is also found at Spizza and Nehaj in Dalmatia, and at Tristyn in Croatia. Deposits of mercury which were formerly of importance, but are now no longer worked, either on account of the competition of other works, or on account of the exhaustion of the deposits, are those of Wolfstein and Moschellandsberg in the Bavarian Palatinate, of Horowitz in Bohemia, of Volterra, Cerigliani, and Ripa, near Serravezza, in the province of Lucca in Italy. Other deposits of subordinate importance in Europe are those of Bagno S. Filippo, Saturnia, Fano, Monte delle Fate, Causoli, Castiglione Chiaverese, Albareto, Marguo, and San Donato di Ninea in Italy, Mires, Santander, Tobiscon and Purchena in Spain, of Neu-marktel in the Santa Anna or Loibel Valley, of Littai (in veins of lead ore) in Carniola, of Balagna and Capo Corso in Corsica, of the Isère, Haute Vienne, and the Sevens in France, of Kongsberg in Norway, and Sala in Sweden.

In North America the most important deposits of cinnabar, the output from which exceeds that of Idria, and in 1901 exceeded that from Almaden, occur in California, in a zone of slates of the Cretaceous and Tertiary period, consisting of talcose, micaceous, clay and siliceous slates, serpentines, sandstones, limestones and dolomites, penetrated by numerous eruptive outbursts. This zone of slate is more or less strongly impregnated with cinnabar in various places, at some of which, especially where serpentine and sandstones are in contact, the proportion of mercury is a very high one, amounting to as much as 35 per cent. The ore occurs both as contact deposits and also disseminated in serpentine and in sandstones. At various places the cinnabar is accompanied by pyrites and bituminous substances. At others it occurs impregnating chalcedony, which may then contain as much as 3 to 10 per cent. of mercury. The deposits occur in a district between the mouth of the Sacramento and Clear Lake (Sulphur Bank and Redlington), upon the eastern slope of the chain of hills extending from San Francisco towards the south-east, known as New Almaden and New Idria, and the coast district about St. Louis Obispo and Santa Barbara. The average yield of mercury was a little less than 0.6 per cent. in 1901.<sup>1</sup> The most important occurrences are those of New Almaden, Santa Clara County, New

<sup>1</sup> *The Min. Ind.*, 1902, p. 556.

Idria, San Benito County, and of Napa Consolidated, Napa County. The occurrence of Sulphur Bank to the east of Clear Lake (now exhausted) was especially interesting on account of its association with an old geyser, which is still throwing out boiling water with considerable quantities of gypsum, alkaline borates, and sulphur. From the sides of some of the fissures in Sulphur Bank, ascending vapours deposited sulphur, which was sometimes intimately mixed with cinnabar. The ore of Sulphur Bank, which contained on an average 1·75 per cent. of mercury, was intermixed with sulphur, and was first worked for that substance.

The Californian cinnabar deposits were known even to the Indians, who used the cinnabar as a paint. Mercury was first extracted by Castellero in 1845. Whilst the deposits of Almaden and Idria seem to become richer in depth, the more important Californian deposits, especially those of New Almaden, seem to be approaching exhaustion. The average output of mercury from calcined Californian ores amounted in 1889 to between 1·088 and 2·295 per cent., according to Randall.<sup>1</sup> Cinnabar has also been found in the States of Texas and Oregon, and also in British Columbia, where it has been worked from time to time. In Mexico, cinnabar is found near Capula and St. Romualdo in the State of Jalisco, at Pedemal, Carro, Dulces Nombres, Guadalupana, and Guadalcazar in the State of San Luis de Potosi, at Huitzuco in the State of Guerrero, and near Zacatecas. Many of these deposits were formerly worked, but do not appear to be in operation at present. The output of quicksilver in Mexico is the second highest in America, and exceeds that of Italy. In South America a deposit of cinnabar, which was discovered in 1566, and was at one time of great importance, occurs in Peru in the district of Huancavelica. The ore occurs in Jurassic strata on the eastern slope of the Western Cordilleras, but is no longer worked. Other South American occurrences are those of Chonta, Cajamarca, and Santa Cruz in Peru, of the State of Tolima in Colombia, and at Andacollo in the Province of Coquimbo in Chili, La Cruz and Santo Tomé in the Argentine Republic, Paranagra, Santa Catherina, Santo Paulo and Oro Preto in Brazil.

In Asia the most important occurrence of cinnabar is in the Province of Kweitschow in Southern China. This is a very extensive deposit, and traverses the province from south-west to north-east. The most important district in which it is extracted is said to be that of Kaitshow in the neighbourhood of the capital, Kweiyang. The works were stopped in the year 1848, but have been

<sup>1</sup> *Eng. Min. Journ.*, vol. 1. p. 265.

restarted recently by an English company. Cinnabar further occurs in Asia in the Province of Hoang Hai in China, at Senday in Japan, at Ildekansk in the district of Nertshinsk in Siberia, in Borneo, Sumatra, Java, and in the neighbourhood of Smyrna.

In Africa cinnabar has been found in various places in Algeria and Tunis.

In Australia it occurs at Cudgegong and Noggriga Creek in New South Wales, Kilkivan in Queensland, and Omaperesee in New Zealand.

The other ores of mercury are of no importance for the extraction of that metal. Amongst them may be mentioned onofrite, a sulphoselenide of mercury, occurring at San Onofre in Mexico; coccinite, an iodide of mercury from Mexico; horn mercury or calomel, a native mercurous chloride, from Moschellandsberg, Avala, Idria, and Almaden. Mercurial fahlore is a fahlore which contains certain quantities of mercuric sulphide. It may contain up to 18 per cent. of mercury. It occurs more especially in Hungary, at Altwasser, Rosenau, Szlana, Kotterbach, Iglo, and Göllnitz, where it contains considerable amounts of mercury, which is extracted from it as a bye-product, at the Stefans Works, near Göllnitz. Many varieties of zinc blende of the Rhine Provinces contain small quantities of mercuric sulphide.

### *Mercurial Furnace Products*

Mercury is extracted not only from its ores, but also from certain furnace products which are obtained in the process of mercury extraction. These consist chiefly of so-called *soot* or "*Stupp*,"<sup>1</sup> which consists of a mixture of finely divided mercury with soot, cinnabar, mercuric oxide, mercuric sulphate, other sulphates, quartz, &c., and of the residues obtained in treating this soot. In gold and silver extraction, amalgams are produced from which the mercury is recovered by distillation.

## EXTRACTION OF MERCURY

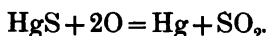
### EXTRACTION OF MERCURY FROM ORES

The extraction of mercury from its ores has up to the present been carried on in the dry way alone. Wet methods have repeatedly been proposed, but have not been able to make any headway, and there is for the present no likelihood of their being introduced. Neither has the electrolytic method of mercury extraction been adopted.

<sup>1</sup> Derived from the Slavonic word *Stupa*, meaning dust.

*The Extraction of Mercury in the Dry Way*

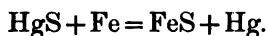
The only ore from which mercury is extracted in practice is cinnabar. Ores containing only native mercury must be looked upon as exceptional; the mercury may be obtained from these by a simple distillation either in retorts or in shaft furnaces. Mercury is extracted from mercurial fahlores as an accessory product, when these ores are calcined. As may be gathered from the previously given chemical reactions of mercury, mercury may be extracted from cinnabar in various ways. Two methods are used upon a large scale. The one depends upon the fact that at a high temperature the oxygen of the air combines with the sulphur of mercuric sulphide, forming sulphur dioxide, whilst the mercury is set free in accordance with the equation :—



The other depends upon heating the mercuric sulphide with lime, when the sulphur combines with the calcium, forming calcium sulphide and sulphate, whilst the mercury is liberated, as shown by the following equation :—



Instead of lime, iron may be employed, as shown in the following reaction :—



In every case, the above chemical reactions take place at temperatures higher than the boiling point of mercury, so that the latter is separated in the gaseous form, and has to be condensed. In the former method the vapours of mercury are diluted by sulphur dioxide, nitrogen, and oxygen, whilst in the latter case, where lime or iron is employed, they are in the concentrated condition, and are, therefore, more easily condensed. Hence the process of mercury extraction may be looked upon as a process of compound evaporation or distillation. According to the above, we have to distinguish :—

1. The extraction of mercury by heating cinnabar in air;
2. The extraction of mercury by heating cinnabar with lime or iron, air being excluded.

As regards the choice of the most suitable process, the preference should, as a general rule, both for economic and for hygienic reasons, be given to the extraction of mercury by heating cinnabar in air, rather than by the employment of lime or iron. Heating cinnabar

in air is a process that may be carried out either in shaft furnaces, reverberatory, or muffle furnaces. When shaft and reverberatory furnaces are used, large quantities of ore can be treated with a comparatively small consumption of fuel and labour; the process can also be so arranged that the workmen are not troubled by the mercurial vapours. On the other hand, the process is open to the objection that the mercurial vapours are diluted by sulphur dioxide, oxygen, and nitrogen, and in the case of shaft and reverberatory furnaces, also by the products of combustion, and that the complete condensation of the mercury is, therefore, rather difficult, consequent losses of metal through incomplete condensation being accordingly unavoidable. The extraction of mercury by heating cinnabar with lime or iron must be performed in retorts. Concentrated mercurial vapours, which can readily be condensed, are thus obtained; but the process is open to the objection that the ores must first be crushed, that only small quantities can be treated, that the retorts last for only a comparatively short time, that the operation is attended with high costs for fuel and labour, and that the workmen are affected by the mercurial fumes when the retorts are emptied out. Although the output of mercury is somewhat higher than in the first-named process, it is nevertheless inferior to it on account of the high working costs, so that it is absolutely unsuitable for poor ores. The chief objection, that the workmen are attacked by the mercurial vapours, is of such paramount importance that the process should really not be carried on at all. It has, therefore, been given up at the majority of works, and has been replaced by the first-named process; its use can only be justified for the treatment of small quantities of ores containing a very high percentage of mercury.

#### EXTRACTION OF MERCURY BY HEATING CINNABAR IN AIR

This process must be regarded as a distillation process, although it might be looked upon as oxidising roasting, and, therefore, a process of combustion, if the metal to be extracted by it were not at the same time volatilised. It consists in heating cinnabar with an excess of air to such a high temperature that the affinity of the oxygen of the air for the sulphur of the mercuric sulphide becomes active, when the sulphur is oxidised to sulphur dioxide, the mercury separating out in the metallic form. A portion of the sulphur dioxide is converted into trioxide by contact action. The cinnabar is best heated to the requisite temperature, as will be shown presently, in shaft or reverberatory furnaces, the mercurial vapour being, therefore, diluted with various gaseous products, from which mixture it has to



be separated, the difficulty being increased by the high temperature of the gases. As has been seen in the extraction of zinc, a metal which is also obtained by a distillation process, the condensation of the zinc vapours, which are also diluted by other gases, forms the most difficult portion of the extraction. At a definite degree of dilution the zinc can no longer be obtained at all in the liquid state, but separates out in the pulverulent condition, a considerable quantity of which afterwards remains in the gases escaping from the condensers. The same occurs in the extraction of mercury, in which the condensation of the metal forms the most difficult portion of the process, in consequence of the dilution of its vapours by the above-named gases, of the high temperature to which the metal has been heated, and of the rapidity with which the current of gas has to pass through the condensing appliances. Nevertheless, the condensation of mercury vapours is more easily effected than that of zinc vapours, because the latter, owing to the low solidifying point of mercury ( $-39^{\circ}\text{C}.$ ), cannot separate out in the form of dust, but, when sufficiently cooled, necessarily forms a liquid, and because mercury can be precipitated without great difficulty, on account of its high specific gravity, even from gases in which it occurs in a high state of dilution. It is, however, unavoidable that comparatively small quantities of mercury—a metal that is volatile at very low temperatures—should escape without being condensed. Even under the best conditions of working, the conversion of some mercury into “*Stupp*” (mercurial soot) is unavoidable. Thus at the works at Monte Amiata only 20 to 30 per cent. of the mercury is got in the form of the metal—the rest is converted into “*Stupp*.” The soot, which consists of a mixture of finely divided mercury, mercurial compounds, and sooty products of the dry distillation of the fuel and the bituminous constituents of the ores, together with its other mineral constituents, forms a deposit in the condensers. It contains up to 80 per cent. of mercury. Its formation is due, according to Patera, to the sulphates, formed when cinnabar is heated, and the chlorides, which were either contained in the ores or produced by the chlorides present in the ash, together with soot, tar, and ammonia derived from organic matters, which substances envelop the particles of mercury as they condense, and prevent them from uniting. The greater portion of the mercury is recovered from the soot by processes to be described later on. The formation of large quantities of soot is a disadvantage in some ways, but, on the other hand, it lessens loss of mercury by enveloping even the most finely divided portions of the metal; and even though it escapes through the condensers, it is caught in the flue-dust chambers.

Apart from the above-named objections, the extraction of mercury by heating cinnabar in the air forms one of the most difficult of metallurgical processes, requiring to be conducted with the greatest care, because considerable losses of metal are necessarily incurred, whilst diseases of the workmen engaged, due to mercurial poisoning, are practically unavoidable. Other difficulties are the penetration of the mercurial vapours into the brickwork of the furnace and condensers; the amount of mercury that remains in the distillation residues unless the utmost care is exercised; the comparatively small proportion of mercury in the ores that have to be treated; the acid character of the condensed water, owing to the sulphur dioxide and sulphur trioxide in the gases carrying the mercury, and its action upon the mercury, as also upon the metal of which the condensers are constructed; together with the further circumstances that mercury forms amalgams with such metals as are little or not at all affected by acid waters, and which would, therefore, otherwise be suitable for the construction of condensers, and the fact that the vapours must be extracted from the furnaces and condensers by means of fans in order to protect the workmen as far as possible. The losses of mercury, which formerly amounted to 50 per cent., and even more at some works, have recently, by a suitable construction of furnace and care in conducting the process, by lining the walls and floors of the condensers, and by suitably constructing the latter, and by proper regulation of the gaseous current, been reduced to 5 to 8 per cent. and even less of the mercury present in the ores. Considering the small proportion of mercury present in the ores (up to 0.3 per cent.), the unavoidable retention of small quantities of mercury in the residues of the latter, the unavoidable formation of soot, the action of acid waters upon the mercury, and the volatility of mercury at ordinary temperatures, the process of the extraction of mercury in its present stage of development must be looked upon as having been very well worked out when the loss is only from 5 to 8 per cent., and it no longer deserves to be considered as an imperfect or crude process as compared with other metallurgical operations. As regards mercurial poisoning, attempts have been made to protect workmen by the employment of suitably arranged fans in front of the condensers, so as to draw off all the gases which formerly escaped from the furnaces and condensers, and by carrying all the gases evolved into stacks, whereby a very marked diminution of mercurial poisoning has been attained. As, however, mercury is volatile even at ordinary temperatures, its vapour rising, according to Brame, up to the height of about 3 feet at 15° C., it will probably never be possible to avoid

altogether the inhalation of small quantities of mercury, which are thus conveyed to the blood through the lungs. Mercury vapours produce disturbances of the nervous system, the digestion, the motor functions, and of the lungs, disease of the teeth, poverty of blood, scurvy and scrofula. When breathed in larger quantities, their effect is fatal. Among the prophylactic measures that have been recommended against mercurial poisoning are the following:—Cleanliness, open air, acid foods, and moderation in the use of alcohol. Melsens<sup>1</sup> recommends the employment of potassium iodide. This is said to render the insoluble mercurial compounds that have been taken into the system soluble, and cause their separation in the urine.

The plant in which the above process is carried out consists of various distillation appliances with condensing attachments. Distillation appliances may be heaps, stalls, reverberatory furnaces shaft furnaces, and muffle furnaces. Distillation in covered heaps with alternate layers of fuel and ore, and the collection of the mercury in the upper layers and in the cover of the heap, a process which was for instance carried out a long while ago at Idria,<sup>2</sup> is a most imperfect process, owing to the volatilisation of mercury, to the retention of a comparatively large proportion of the metal in the ores, and to the penetration of the metal into the ground. At present it only possesses historical interest. For the same reasons, stalls are unsuitable for the extraction of mercury. They are used exceptionally in the calcination of mercurial fahlores for the extraction of copper and silver. In this process the mercury is condensed as a bye-product in the upper layers of minerals, and is obtained by washing the latter. At the Stephans Works in Upper Hungary, mercurial fahlores are calcined in circular stalls, in heaps of 50 tons upon a bed of wood with a layer of charcoal above it. The calcination lasts four weeks. The mercury, extracted by washing the upper layers of ore, is purified by distillation.

Shaft and reverberatory furnaces are used both for lump ore and for small ore. Externally fired shaft furnaces for lump ore consist of an empty shaft, whilst for small ores the shaft is fitted with inclined slabs or plates. Formerly all of these furnaces used for lump ore were worked intermittently. At present, at most works, intermittently worked shaft furnaces of this type, in which small ores, properly agglomerated, can also be treated, have been replaced by the much more economical continuous-acting furnaces. As a rule

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1877, p. 236.

<sup>2</sup> *Mitter, Vortrag auf dem Bergmannstag zu Klagenfurt*, 1893.

externally fired shaft furnaces, working continuously, should be used for smalls that do not form dust. Under certain circumstances, as when the cinnabar permeates the whole mass of the ore, and when the ore readily decrepitates, lump ore is pulverised to some extent and treated as small ore. Externally fired shaft furnaces would be used for lump ores if cheap uncarbonised fuels are available, whilst pure carbonised fuel, *e.g.*, charcoal, is dear. When cheap carbonised fuels are obtainable, the shaft furnace proper, in which the fuel is in direct contact with the substances to be heated, would be preferred to the continuous working shaft furnace externally fired, on account of the smaller formation of soot. Reverberatory furnaces, which were frequently employed, are inferior economically to externally fired shaft furnaces, as they require both more fuel and more labour than the latter. They are therefore only employed in those cases in which the shaft furnaces are not suitable, *viz.*, in the case of small ore which forms much dust, of certain varieties of soot, and of lump ores that decrepitate in the shaft furnace.

Shaft furnaces proper, in which the ores are charged together with charcoal, have been in use for some time (Hähner furnace), but have recently received important improvements (Novak and Spirek furnaces), and have, for example at Idria, replaced the modern externally fired furnaces for lump ores. In their construction they do not differ essentially from the externally fired shaft furnaces for lump ores, and are to be recommended on account of the small production of soot in those cases in which lump ores and cheap carbonised fuels, such as charcoal, are obtainable. These carbonised fuels form no soot, whereby the formation of mercurial soot ("*Stupp*") is lessened. Muffle furnaces were largely employed at one time, but have now been replaced at most works by reverberatory and shaft furnaces. The muffles were at first made of clay, but later iron has been used with advantage. These furnaces present the advantage that the mercurial vapours are not diluted by the products of combustion of the fuel, as occurs in the case of reverberatory and shaft furnaces, nor are they overheated, so that they can be readily condensed and therefore require less extensive condensing appliances. The extraction of mercury when the process is properly carried out is also somewhat higher in consequence of the diminished production of soot. On the other hand, these furnaces are liable to the objection of higher labour costs and of a high consumption of fuel, as also to the very serious objection that the workmen suffer more from mercury vapours than in the case of reverberatory and shaft furnaces. As, therefore, they are at least equalled in economic respect by the

modern furnaces of the latter type, even when not surpassed by them, they have disappeared from most works, and, on account of the above reasons, their use should be discouraged.

### *Condensing Appliances*

These ought to be manufactured of a substance which does not take up mercurial vapours, is a good conductor of heat, is capable of being moulded into the required shapes, and is able to resist the action of acid vapours and liquors, as also of the mercury itself. No one has as yet, however, succeeded in discovering a material answering to all these requirements. Of the substances used up to the present iron is the easiest to mould and the best conductor of heat, but does not resist the action of acid vapours for any length of time. Brickwork absorbs mercurial vapours, is a bad conductor of heat, and is attacked by acid liquors. Wood has sufficient resisting properties, but is a bad conductor of heat. Glass has not been found applicable by itself, but only in combination with wood. The most suitable material up to the present has been found to be stoneware. This is capable of resisting mercury and acids, and may be had so thin that its low conductivity for heat need not be taken into account. Stoneware is used in the form of pipes. In addition to stoneware, all the above-named substances are used, as also are vessels of burnt and glazed clay. Iron is protected by a coating of cement against the action of acid vapours and waters. The form which condensers assume is either that of a series of tubes or of chambers. Clay and stoneware are used in the former shape, iron and wood in both forms, brickwork and glass in the form of chambers. In many cases condensation in tubes is combined with condensation in chambers. The diameter of the tubes and the dimensions of the chambers must be confined within definite limits, as tubes which are too small interfere with the draught, whilst chambers which are too large have but little cooling effect upon the inner portion of the current of gases traversing them. By a suitable combination of tubes and chambers, or by chambers of different material, as also by means of brick chambers cooled by cast-iron boxes, through which water circulates, the losses of mercury by imperfect condensation have recently been brought down to a very small amount. The condensers of Czermak, to be described later, combined with flues or chambers of wood, have proved most suitable. The condenser is made of iron, lined with some suitable material to enable it to withstand the action of acid water and vapours. Mitter has introduced

stoneware in the construction of these condensers. A good draught in the furnaces and condensers, which is quite indispensable, may be obtained either by means of powerful stacks heated by separate fireplaces, or else by exhausting machinery of various kinds, such as water blast, Cagniardelle's blowers, or fans. The draught must be such that the pressure of the current of gas in the furnace and condensers must be brought down below the pressure of the atmosphere, so as to prevent the mercurial vapours escaping from the apparatus. In ordinary working the pressure of the gases issuing from the furnace into the condenser is less than atmospheric pressure by an amount equivalent to 4 inches of water. Draught produced by stacks heated by separate fireplaces was formerly employed, but has now been given up in favour of fan suction, owing to the uneven action of the former and the imperfect condensation of the vapours and consequent injury to the workmen which that method entails.

Mercury is transported in flasks of wrought-iron closed by a screw stopper. The weight of mercury in a full bottle amounts in Idria and Almaden to 76 lb., in California to 76.5 lb. In the smaller European works mercury is shipped, as was formerly done also at Idria, in bags of sheepskin containing 55 lb.

The various distillation furnaces and the condensing appliances connected with them, the mode of conducting the process, and the economic results obtained, will now be considered in detail. For the sake of maintaining the proper sequence it is advisable to consider first the extraction of mercury in externally fired furnaces ("Flammöfen"), shaft or reverberatory, then in shaft furnaces proper, and finally in muffle furnaces.

### *The Extraction of Mercury in Externally Fired Furnaces*

Externally fired furnaces may be divided into those with a shaft-like laboratory chamber, so-called externally fired shaft furnaces, and reverberatory furnaces with a horizontally placed laboratory chamber, or true reverberatory furnaces. Externally fired shaft furnaces are generally used for the extraction of mercury, being employed for lump ores wherever raw fuels are cheap and carbonised fuels dear, and for small ore whenever it does not form too much dust. Reverberatory furnaces are used only for those ores which are not suitable for treatment in shaft furnaces, either on account of the large amount of dust in the case of small ore, or on account of their ready decrepitation in the case of lump ores.

*Extraction of Mercury in Externally Fired Shaft Furnaces*

These may be divided into furnaces working intermittently and furnaces working continuously. The former kind are still in use, but are far inferior to the latter as regards their economic results. In future, therefore, continuous working furnaces should as a rule be employed.

*Extraction of Mercury in Shaft Furnaces Working Intermittently*

These furnaces were formerly in use at Idria and at the Redington Works in California, but have been given up on account of their expense. They are still used upon a large scale at Almaden, in Spain. At New Almaden, in California, they were used for a considerable period, but have now been given up. These furnaces can only be employed for ore fines, when these are charged in shallow vessels known as *cassettes*, or when they have been agglomerated into bricks. The furnaces consist of shafts fired either internally or laterally. The condensing plant consists either of a series of flask-shaped clay pipes or of brick chambers. The fuel used must be uncarbonised, such as brushwood, wood, or coal. The draught is produced by stacks, or better still by fans. The whole amount of ore to be treated is charged at one time into the furnace, and is heated by firing up until it continues to burn by itself owing to the heat developed by the oxidation of the sulphur in the cinnabar; after the fire has burnt out the furnace is left for some time to cool, when the distillation residues are removed and a new charge introduced.

*Furnaces Fired Internally*

According to the system of condensers connected with these furnaces, they are distinguished into so-called Bustamente furnaces, the condensing appliances of which consist of a series of flask-shaped clay pipes, known as *aludels*, followed by chambers, and so-called Idrian furnaces, the condensers of which consist of a series of brick chambers. The furnaces are 20 to 30 feet in height, and circular or square in section, the diameter of the former being from 4 feet 3 inches to 6 feet 6 inches, and the side of the latter 10 feet. In the interior of the furnace there is a perforated arch which separates the fire-space from the distillation chamber above the arch. In order to diminish the pressure of the column of ore upon the side walls of the furnace, or in order to be able to place trays with ore fines conveniently in the furnace, perforated arches have also been introduced in the distillation chamber of the furnace.

*The Bustamente Furnace or Aludel Furnace*<sup>1</sup>

This furnace was designed in the year 1633 by a medical man, Lopez Saavedra Barba, in Huancavelica, in Peru, and introduced in the year 1646 into Almaden, in Spain, by Bustamente, whose name it bears. In the latter place it has maintained itself up to the present in spite of many attacks. There are at Almaden 22 Bustamente furnaces, which furnish by far the greater portion of the mercury production of that place. In the middle of the eighteenth century,

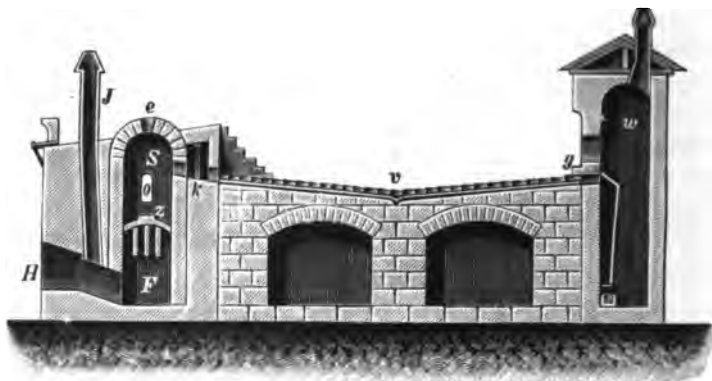


FIG. 264.



FIG. 265.

this furnace was introduced into Idria by Poll. Here, however, the aludels were soon replaced by brick chambers, whereby the Bustamente furnace was converted into an Idrian furnace.

The construction of the Bustamente furnace, together with the condensing appliances used at Almaden, is shown in Figs. 264 and 265. A pair of these furnaces is united to form a block. *S* is the cylindrical shaft, 20 to 26 feet high, the diameter of which for the

<sup>1</sup> Kuss, *Mines et Usines d'Almaden*; *Annales des Mines*, 1878; *État actuel de l'Usine d'Almaden*, Ann. des. Min. 1877; Escosura, *Historia del Tratamiento Metalurgico del Azogue en Espana*, Madrid, 1878; Gandolfi, *Les Mines et Usines d'Almaden*, Rev. Univ. des Mines et de la Métall., 1889.



smaller furnaces amounts to 4 feet 3 inches, and for the larger to 6 feet 6 inches. *Z* is a perforated brick arch, beneath which lies the fire-place *F*; above it is the distillation chamber. The upper part of the furnace is closed by a hemispherical arch, in which there is a charging door, *e*. The ores are first charged by means of the opening *O*, in the side wall of the furnace, which is bricked up before the commencement of the operation, and later on through the above-named charging door *e*, which is closed by a cover, luted with moist ashes. *H* is the fire door through which the air required for oxidation also enters. *J* is a stack to carry off any products of combustion that do not ascend through the furnace; the greater part of these, however, ascend through openings in the brick arch and penetrate, together with an excess of air, through the column of ore lying upon the arch. The products of combustion, together with the mercurial vapours and sulphur acids evolved in the distillation chamber, pass through six openings, *K*, in the upper portion of the shaft, each of which is 12 inches high and 4 inches broad, into the condensers.

The condensing appliances consist of 12 strings or rows of aludels lying side by side, and of two chambers, with each of which six rows

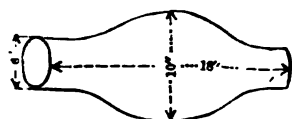


FIG. 266.



FIG. 267.

of aludels communicate. The aludels, one of which is shown in Fig. 266, consist of flask-shaped clay tubes, glazed on the outside, 16 inches to 18 inches long, 8 to 10 inches in diameter at the widest part, and  $4\frac{1}{2}$  inches to 6 inches in diameter at the extremities. The object of the flask-like shape is to diminish the velocity of the gaseous current and thus to promote the condensation of mercury; 40 to 45 of these aludels are connected together, as shown in Fig. 267, so as to form a continuous tube. In order to prevent the escape of gas at the points of union, they are carefully luted. The rows of aludels lie parallel to each other in grooves in two surfaces sloping towards each other, so arranged that the first half of the row of aludels leads the gases and vapours downwards, and the second half conveys them upwards. The aludels that lie upon the descending half have each in the bottom of their widest portion an opening 0.08 to 0.16 inch in diameter, through which the mercury condensed in them escapes. This opening is omitted in the aludels of the ascending half. The condensed mercury,

part of which escapes from the above-mentioned holes, and part of which is emptied out from time to time from the aludels into the inclined grooves, run into the inclined channel, *v* (Figs. 264 and 265), in which it collects, and flows from it into the pans, *s*, from which it escapes by means of the iron pipe, *f*, shown in Fig. 268, into a storehouse, where it is collected in graduated cast-iron pans, one of

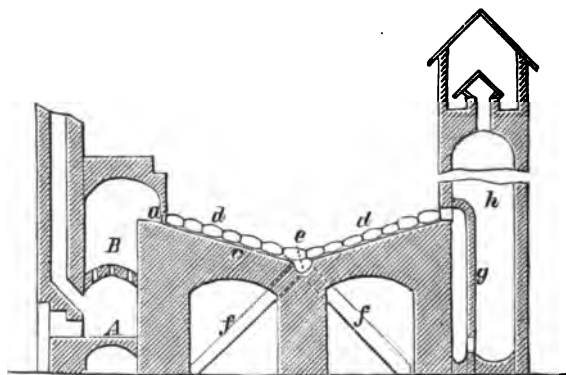


FIG. 268.

which is provided for each pair of furnaces in the block. From the row of aludels the vapours and gases pass into condensing chambers, *w* (*h* in Fig. 268), built of brick, in which any mercury vapours not yet condensed are to be deposited. A partition wall, *g*, is

introduced so as to lengthen the path of the vapours. Any gases not condensed escape into the stack, which is provided with a damper. The fuel used at Almaden was formerly brushwood, but is now coal. The charge for the larger furnaces is 13 tons of ore, for the smaller furnaces 8·7 tons. Together with this quantity 1·5 tons of small ore, moulded into bricks, known as *bolas*, are charged in each furnace. Four classes of ore are distinguished at Almaden, viz, *metal*, rich ore; *requiebro*, medium ore; *china*, poor ore; and *vacisco*, small ore. According to Escosura, the average consumption of these classes is as follows:—

	Metal.		Requiebro.		China.		Vacisco.	
	1	2	1	2	1	2	1	2
Cinnabar . . . . .	29·1	21·2	13·3	10·2	1·2	0·86	5·1	2·8
Iron pyrites . . . . .	2·2	2·0	2·0	1·9	2·1	2·8	12·3	1·5
Bituminous matter.	0·6	1·0	1·0	1·2	3·4	0·9	4·6	0·7
Gangue . . . . .	67·5	74·8	82·1	85·6	90·2	93·5	77·5	93·3
<b>Total . . . . .</b>	<b>99·4</b>	<b>99·0</b>	<b>98·4</b>	<b>98·9</b>	<b>98·9</b>	<b>98·06</b>	<b>99·5</b>	<b>98·3</b>
<b>Metallic mercury .</b>	<b>25·5</b>	<b>18·28</b>	<b>11·47</b>	<b>8·64</b>	<b>1·03</b>	<b>0·75</b>	<b>4·40</b>	<b>2·41</b>

Before the ore is charged, the perforated arch is covered with a layer 2 feet deep of fragments of quartz or of poor lump ore (*solera pobre*), the pieces of which are such a size that the flame from the fuel can penetrate through them readily. Upon it ores of medium quality (*requiebro*) are charged, and upon this the poorer ores (*china*), which two kinds together amount to two-thirds of the total charge. Rich ore (*metal*) follows, upon which fragments of old aludels and blocks of fine ore (*vacisco*) and residues from soot treatment are placed; three men are occupied in charging, which takes  $1\frac{1}{2}$  to 2 hours. As soon as the whole charge has been introduced into the furnace, the two charging doors are closed, and the fuel in the firing chamber is ignited. Formerly brushwood was used as fuel, but now coal is employed, which is burnt upon a grate. After 4 to 5 hours the first mercury shows in the front aludels. After firing from 10 to 12 hours, the column of ore has been heated sufficiently to be able to supply the heat required for the continuance of the process by the combustion of the sulphur in the cinnabar; firing is therefore discontinued. The air which serves to oxidise the sulphur is heated by its passage through the perforations of the arch and of the barren ore lying upon it to a temperature of  $200^{\circ}$  to  $300^{\circ}$  C. The ores burn for 43 or 44 hours, during which time mercury distils uninterruptedly. After the end of this second stage (*brasa*), the residues in the furnace are allowed to cool for some 18 hours, to promote which the doors of the fireplaces and the charging doors are opened. At the end of this time the distillation residues are drawn from the furnace, which occupies some 2 hours, after which the furnace is re-charged. Each campaign lasts upon the whole some 3 days of 24 hours; of this time, 10 hours are occupied in firing, 44 in the distillation, and 18 in the cooling. Formerly a charge consumed from 2.2 to 2.5 tons of fuel. Nowadays, owing to the employment of coal, a large furnace, taking a charge of 13 tons of lump ore and 1.5 tons of ore fines, requires 18 cwt. of coal, whilst a small furnace, taking 9 tons of lump ore and  $1\frac{1}{2}$  tons of fines, requires 14 cwt. of coal. As regards the temperature in the condensers, it has been found, according to Kuss, that the highest temperature in the first aludels is from  $245^{\circ}$  to  $260^{\circ}$  C., which is attained after 40 hours. In the tenth aludel from the furnace it reaches  $105^{\circ}$  C. at the end of 48 hours; in the midmost aludel of the row it amounts to  $50^{\circ}$  at the end of 52 hours; whilst in the last aludel of each row it rises to  $29^{\circ}$  at the end of 52 hours. The aludels which lie on the slope next to the furnace are cleaned out every month, those on the other slope every two months, to remove the mercury and soot contained in

them. For this purpose the luting is removed and the aludels are held one by one vertically over the inclined gutters of the slope upon which the aludels lie, in order that the mercury contained in them may run into these gutters. The soot is then removed from them by means of brushes. It is collected in heaps, and treated in the manner to be described later on. The residues resulting from its treatment are moulded into blocks, together with ore fines, and treated in the furnace just described. Opinions vary as to the loss of mercury, which is given as between 4.41 and 25 per cent. According to L. de la Escosura,<sup>1</sup> Langer<sup>2</sup> calculates that the loss of quicksilver, when modern methods of assay are employed, averages 20 per cent. As already stated, the aludel furnace is in use nowhere else, and in fact at Almaden its days are numbered, for Czermak-Spirek furnaces are being erected there. It requires no proof that the intermittent process carried on in it is inferior to a continuous one. On the other hand, the condensing arrangement of rows of aludels followed by chambers represents a principle which has been quite recently acknowledged as the correct one, although in modified form. The newest and best condensers have been arranged on this system in Idria, and consist of a series of stoneware pipes followed by wooden chambers.

### *The Idrian Furnace*

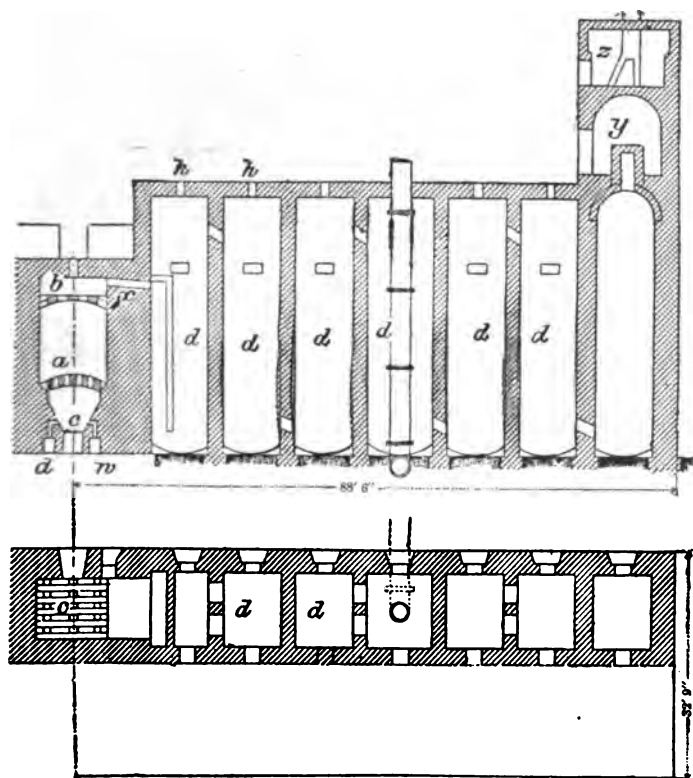
This furnace is distinguished from the Bustamente furnace only by the construction of the condenser, which consists here not of aludels but of chambers lined with cement, six or eight of which are built on either side of the furnace. The gases and vapours, therefore, escape at both ends of the shaft. The Idrian furnace was designed in 1787 by von Leithner at Idria, and has been in use there, with various modifications, up to the year 1870. It was introduced in the year 1806 by Larrañaga into Almaden, and is still in use there, side by side with the Bustamente furnace. The original furnaces were rebuilt at Idria in 1825, either a pair or a single one forming a furnace block.<sup>3</sup> The double furnaces were called Franz furnaces; and quadruple furnaces, containing four in one block, Leopoldi furnaces. The construction of the modern Leopoldi furnace at Idria is shown in Figs. 269 and 270, in which the condensing chambers on one side of the furnace only are shown. The furnace is square in plan, 10 feet in the side, and is furnished with two perforated brick

<sup>1</sup> *Op. cit.*, p. 448; Kuss, *op. cit.*

<sup>2</sup> *Beschreibung des Quecksilbergewerkes Almaden.* *Berg- und Hüttenm. Jahrb. d. Berg.-Akad.*, 1879.

<sup>3</sup> Mitter, *loc. cit.*

arches. Upon the lower one, *a*, lump ores are placed, whilst the upper one serves to carry the clay or cast-iron pan in which the fine ore is charged. At one time, furnaces with three perforated arches in the shaft were employed. The fireplace is under the bottom brick arch, and is provided with a firegrate *c*, *w* being air-flues; *h* are manholes for cleaning out the chambers; *x* are the escape flues, of which there are six on either side of the furnace;



Figs. 269; 270.

the bottom of the condensing chambers, *d*, slopes towards one side, in order to allow the condensed mercury to flow off into a gutter running along one side of the chambers, which conveys it into the magazine. From the last chamber the gas passes through the flues *y* and *z* to the stack. The construction of the older form of double furnace with three arches is shown in Figs. 271 to 273, of which Fig. 273 shows the shaft on a somewhat larger scale than that of the other two figures. The lump ores are charged upon the bottom arch *x*, *x*;

upon the middle one, *y, y*, ore of medium size is charged; and upon the top arch, *z, z*, the pans with ore fines; *w* are the outlet flues, of which there are six on either side of the furnace, and *T* the condensing chambers connected with them. From the last and highest condensing chamber, *u*, the gases pass into the flue, *K*, leading to the stack. On either long side of the system of chambers there are

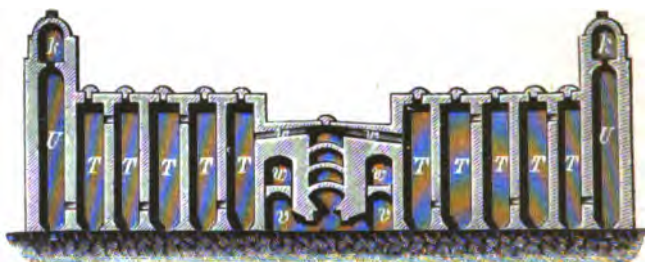


FIG. 271.

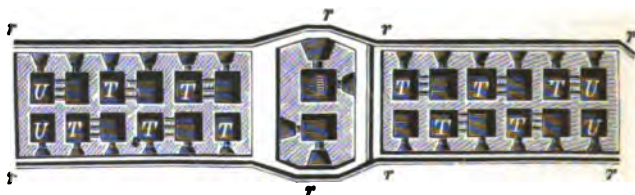


FIG. 272.

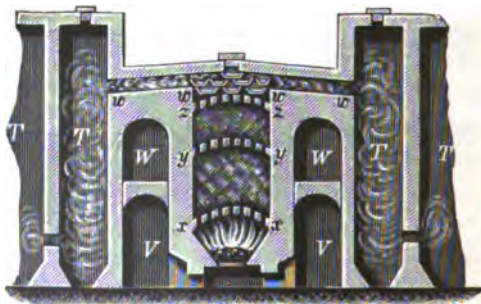


FIG. 273.

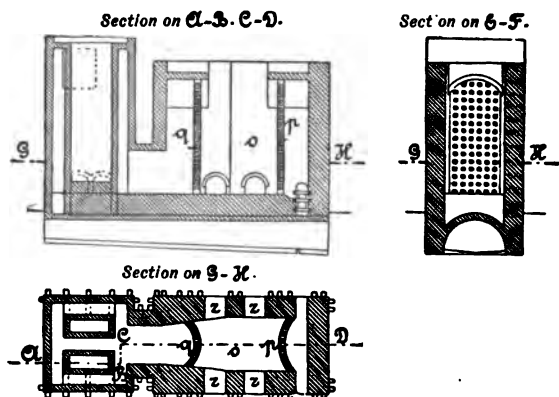
gutters, *r*, which collect the mercury from each chamber (the bottom of which slopes towards the gutter), and which lead it to the magazine. *V* and *W* are archways through which the air passes into the shaft or to the fuel. At one time only ore fines were treated in these furnaces and were charged in pans, of which the furnace contained 1,800, with 44 lb. of ore in each. This furnace was first fired for 10 to 12 hours, then it was left to itself for 5 or 6 days, after which the distillation

residues were removed. The charge of ore per furnace amounted to 49 to 58 tons; the output of mercury was 2·36 per cent. when ores containing 3·26 per cent. were treated. This output was smaller than in the case of the aludel furnace, but, on the other hand, the working expenses were also less. At present there are two Idrian furnaces in use at Almaden, though they are likely to be supplemented soon. Each of them is 25 feet high, and is circular in plan, with a diameter of 10 feet. As in the case of the aludel furnace, there is here only one single brick arch with perforations. There are five openings on either side in the upper part of the shaft, through which the gases and vapours escape into the condensing chambers, of which there are six on either side. As in the furnace at Idria, the last chamber is higher than the others, and acts as a stack. The other details of the chambers, the sides and floor of which are coated with Portland cement, are similar to those at Idria. The charge of these furnaces is twice that of the Bustamente furnace, viz., 27·2 to 28·5 tons of ore. The labour employed for charging the furnace is the same as for the Bustamente furnace; it occupies one day. The furnace is then fired for a day, the heat necessary for distillation being maintained during the two following days by the sulphur contained in the ore. The period of cooling, which lasts for a day, now follows, and another day is occupied in withdrawing the residues after distillation and the ashes of the fuel. Including charging and clearing, six days are, therefore, required for distillation. The consumption of wood for each distillation amounts to 4·2 to 4·5 tons. The soot is freed by rubbing in the condensing chambers from the greater part of the quicksilver contained in it. The residues thus obtained are agglomerated, together with ore fines, into lumps, and treated in the distillation furnace. According to experiments executed at Almaden, the losses of mercury in this furnace are higher than in the Bustamente furnace, the ratio being given as 6·2 in the former to 4·41 in the latter. These results have, however, been obtained by the old method of ore assaying in retorts with the addition of lime, and can, therefore, not be taken as reliable. On the other hand, it is perfectly clear that the working of the Idrian furnace is cheaper than that of the Bustamente furnace.<sup>1</sup> In Idria, where the furnaces had done better work than the Bustamente furnace, especially for ores poorer in mercury than those of Almaden, carrying 3 to 4 per cent. of mercury as against 7 to 10 at Almaden, this furnace has been thrown out of use since 1870, and has been replaced by continuous working furnaces and modern shaft furnaces.

<sup>1</sup> Langer, *loc. cit.*

*Externally Fired Furnaces*

Furnaces of this type were formerly in use upon a large scale at the Redington works, near Knoxville, and the New Almaden works, both in California, but have been replaced by modern furnaces.<sup>1</sup> The last furnace of this kind was in partial use in New Almaden in the year 1889, but has disappeared by this time. In this furnace the fireplace was built out on one side of the shaft, this side being formed by a curved perforated wall, through which the products of combustion could enter the shaft, after which they passed through horizontal channels left in the column of ore, towards the opposite side, through which they were discharged into condensing chambers. The latter were similar to those used in the Idrian furnaces; they were, however, confined to one side of the furnace, and were present in



FIGS. 274—276.

larger numbers (from 18 to 22), terminating in a brick tower, which was again connected by means of a flue with a Guibal fan. Lump ore, as well as ore fines moulded into blocks, were treated in this furnace. Its construction is shown in Figs. 274 to 276; *o* is the shaft furnace proper, *p* and *q* are brick walls perforated to their full height for the passage of the flames. They are arched in plan so as to better resist the lateral pressure of the column of ore. The fire-grate is in a chamber behind the side wall, *p*, through openings in which the flames penetrate into the shaft, and, mixed with the vapours of sulphur dioxide and mercury, pass through openings in the wall, *q*, into the condensing appliances. The passage of the gases through the column of ore is facilitated by means of channels left in

<sup>1</sup> Eggleston *Metallurgy of Silver, Gold, and Mercury*, vol. ii., p. 814.



them, corresponding to the openings in the walls of the furnace. When lump ore was treated, these channels were produced by a suitable arrangement of the lumps of ore. When both lump ore and blocks of ore fines (*adobes*), or ore fine blocks alone were being treated, the channels were constructed of these blocks. In the upper part of the ore column these channels were of a smaller section than in the lower part, in order to cause the flames to travel as nearly horizontally as possible through the furnace. The ores are let down in baskets through the furnace mouth. The residues remaining after the mercury has been distilled off are removed through the apertures, *z, z*. The top of the ore column is sealed by a cover of old iron, straw, and clay. In the first condensing chamber there are two smaller chambers for drying the ores; they are open at their upper ends, and provided with two apertures each at their lower ends for drawing out the dried ores. The furnace is 18 feet high, 9 feet broad, and 12 feet long. The opening through which gases and vapours pass into the first condensing chamber is 7 feet high. The charge amounts to 90 to 100 tons, the older furnace taking charges of 50 to 70 tons only. Charging takes a day, and requires the labour of eight men. After the furnace is properly closed up, firing is continued for  $4\frac{1}{2}$  days. The mercury commences to condense at the end of 14 or 16 hours, and has finished after  $4\frac{1}{2}$  days. The furnace is then allowed to cool for  $3\frac{1}{2}$  days, during which time the doors of the fireplace are opened. After this time, the cover is removed and the distillation residues drawn out through the openings provided for that purpose. One man per shift is required to look after the fire. The cleaning out of the furnace takes a day and requires four men. Three charges can be worked per month. Eighteen cords of wood are required for 100 tons of ore. Upon the average, each ton of ore yielded 1,873 flasks of mercury. These furnaces have been replaced in California by continuous working furnaces, which work much more cheaply and do not require the ore fines to be moulded into bricks.

#### *The Extraction of Mercury in Shaft Furnaces Fired Continuously*

To this class of furnace belong the furnaces of Exeli, of Langer, of Knox, of Hüttner and Scott, of Livermore, of Czermak, and of Czermak and Spirek. The furnaces of Exeli and Langer are suitable for the treatment of lump ores. The furnaces of Hüttner and Scott, namely, the Granzita furnace and the Tierra furnace, as also the Czermak and Czermak-Spirek furnace and the Livermore furnace, are suitable for the treatment of ore fines. The Knox furnace can

treat both lump ores and a mixture of lump ores and ore fines, provided that the latter do not exceed a definite proportion of the whole. The most efficient of these furnaces are those adapted for the treatment of ore fines, hence under certain circumstances they are used for treating pulverised lump ore. Both the furnaces of Exeli and Langer have given good results with lump ore. That of Knox, which was favoured for a long time in California, is now quite out of use. All the furnaces which have been mentioned as suitable for ore fines, of which the Hüttner and Scott and Livermore furnaces were invented in California, are at present in use at various works and give satisfactory results.

### FURNACES FOR LUMP ORES

#### *Exeli Furnace*<sup>1</sup>

This furnace was built at Idria in 1872 by Exeli. It consists of a shaft furnace, surrounded with three external fireplaces, and cased in wrought-iron to prevent loss of mercury; there is also an iron plate underneath the bottom of the furnace. The construction of the furnace is shown in Figs. 277 and 278; *S* is the furnace shaft with the three fireplaces, *a*, and three openings underneath them, *b*, for the removal of the distillation residues. The residues drawn through these openings are cooled in the chamber, *c*, which serves at the same time as an ashpit, wherein they may give up their heat to the air entering under the grate. In order to remove the distillation residues from the furnace, the necessary tools can be introduced through the doors, *d*, into the openings, *b*. The charging apparatus consists of a cup and cone with water seal. The vapours escape through the pipe, *e*, into condensers. The grates are arranged for wood firing. The shaft is 13 feet high, 6 feet 3 inches in diameter in the upper part, and 4 feet 3 inches in the lower part. The grates are each 34 inches long and 12½ inches wide.

The condensing arrangement consists of cast-iron Y-shaped pipes 19 inches in diameter, followed by condensing chambers, the arrangement of which is shown in Figs. 279 and 280, in which *g* are the pipes, three rows of which lie side by side. They terminate below in short vertical branches, which are open and dip into boxes, *h*, 19 inches wide, filled with water. In these the condensed mercury collects and flows off into an iron vessel, which is kept locked. The tubes are cleaned from soot by means of discs attached to rods,

<sup>1</sup> *Das K. K. Quecksilbergwerk Idria in Krain, Wien, 1881.*

introduced through the upper portion of the tubes, by means of which the soot adhering to the insides of the tubes is pushed down into the boxes, *h*. This furnace treated ores that would not pass through a sieve of 0·8 inch mesh, and which contained from 0·2 to 0·8 per cent. of mercury. In 24 hours 14·4 tons of ore were treated with a consumption of 102 cubic feet of cord wood. The distillation

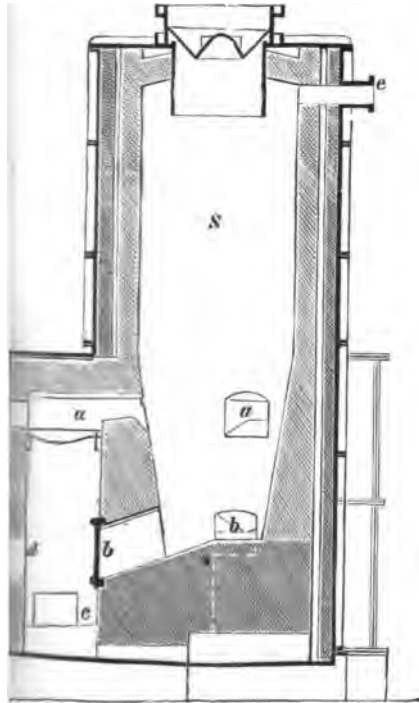


FIG. 277.

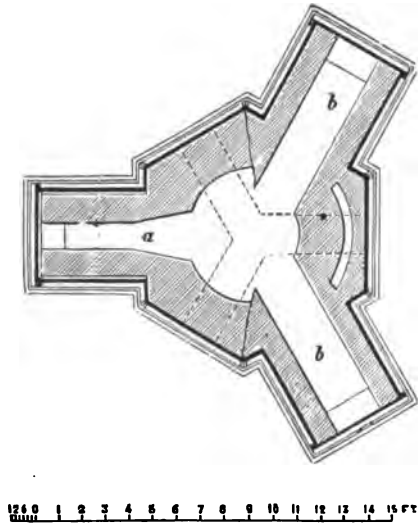
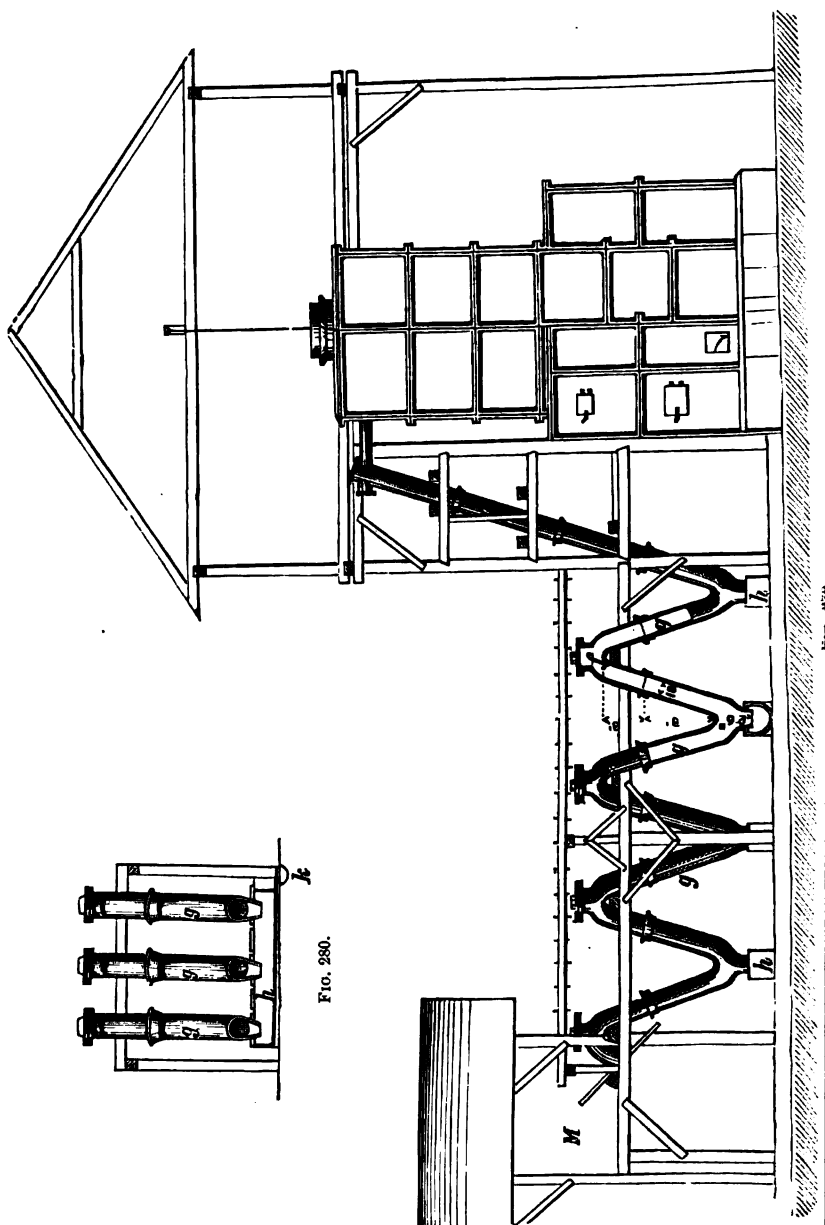


FIG. 278.

residues contained 0·002 per cent. of mercury, the total loss of metal amounting to 8·9 per cent.

By building up the fire spaces, these furnaces were afterwards converted at Idria into true shaft furnaces, in which the fuel—charcoal—was introduced together with the ores into the shaft. The Exeli condenser was open to the objection that in consequence of the inclined position of the cast-iron pipes the acid water that condensed in them ran down into the lower portion and rapidly destroyed this part. Czermak, therefore, employed, instead of the inclined pipes, vertical pipes lined inside with cement, the lower portion of which terminated in iron boxes, which were also protected by a layer of cement. This

condenser has been replaced by the modern Czermak condenser,



which effectively employs the principle of surface condensation by subdividing the mercurial vapours among several rows of narrow

stoneware pipes. At present, therefore, as fast as the iron pipes become destroyed they are replaced at Idria by pipes of glazed stoneware.

There are two Exeli furnaces at work in New Almaden, which were built in the years 1874 and 1875. The construction of the first built furnace is shown in Figs. 281 and 282. The shaft<sup>1</sup> is altogether 20 feet high in the clear; the diameter in its uppermost widest part amounts to 11 feet 6 inches, narrowing down to 5 feet 6 inches; whilst in the bottom portion, 8 feet in height, it narrows still further down to 4 feet. The shell consists of wrought-iron,  $\frac{1}{8}$  inch

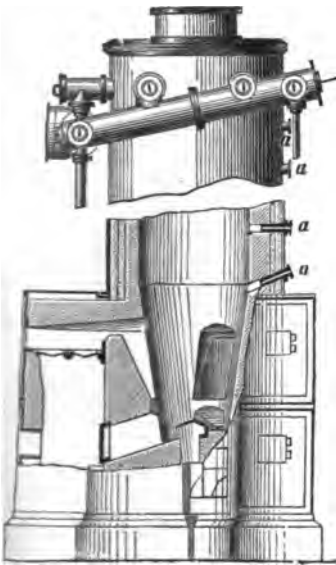


FIG. 281.

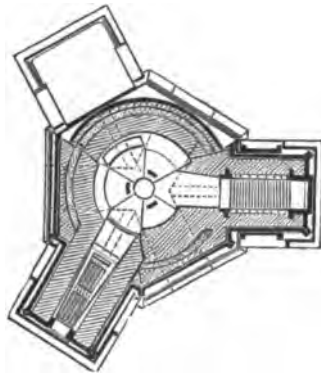


FIG. 282.

thick. It encloses first of all a shaft of common brick, and then an inner lining shaft proper of fire-brick separated from the former by a small interspace. The lower portion of the furnace, in which the charging and discharging doors are situated, is supported on cast-iron plates. The furnace stands upon a plate of cast-iron, forming a very shallow cone, so that any mercury collecting in it runs into a vessel placed under the apex of the cone. The furnace top is closed by an annular plate of cast-iron, all except the throat, which is fitted with a charging apparatus similar to that already described. When the furnace is charged, a height of 3 feet is left empty in the upper part. In this

<sup>1</sup> Egleston, *loc. cit.*

the vapours evolved during distillation collect, and escape through cast-iron pipes 1 foot in diameter, of which there were six in the earlier furnace, but only three in the later one, into a main 21 inches in diameter inclined at an angle of  $10^{\circ}$ , through which they pass into the condensing chambers. All these tubes are fitted with cleaning discs, in order to be able to remove the soot. So as to be able to observe the progress of the distillation, there are twelve peep-holes, *a*, arranged at four different heights. The condensing appliances consisted formerly of brick chambers, a Fiedler condenser, and Fiedler-Randol glass and wood condensers. The brick chambers, of which there were two to each furnace, were 28 feet high, 28 feet long, and 18 feet broad. Each of these was divided into halves by means of a partition. From these chambers the gases passed into a Fiedler condenser, the construction of which is shown in Figs. 283

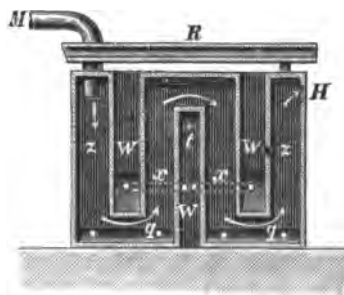


FIG. 283.

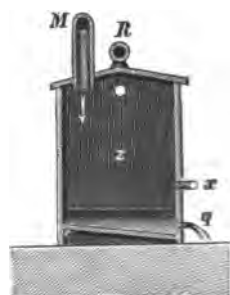
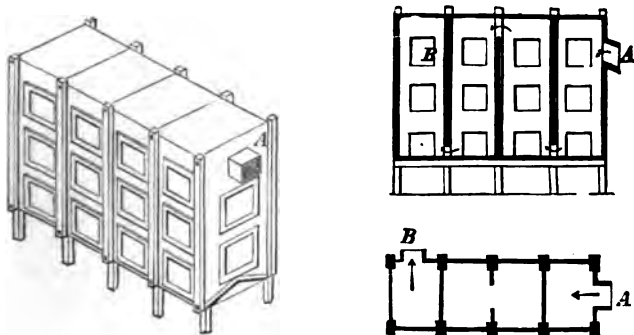


FIG. 284.

and 284, and which consisted of rectangular boxes of cast-iron, 10 feet 6 inches long, and 5 feet 6 inches high and broad, the cover of which is shaped like a flat roof. It was divided into four divisions *Z*, by means of three hollow iron walls, *W*, in which water circulated, each division having an inclined bottom. The first and last of these iron walls were open above. Through the pipe, *R*, the water entered the hollow walls, which communicated with each other by means of a small pipe, *x*, and after flowing through these it escaped through the opening *t*. The pipe, *R*, also served to cool the iron roof and side walls of the boxes. The gases entered the boxes through the pipe *M*, traversed the divisions, and escaped at *H*, the products of condensation escaping through the pipe *q*. According to Egleston, this arrangement was done away with, in spite of the good results obtained from it, because it interfered with the draught of the gases and vapours, and because the iron of which it was made was strongly attacked by the condensed vapours.

The older condensers of glass and wood into which the gases passed from the Fiedler condenser are shown in Figs. 285 to 287. They consisted of rectangular wooden boxes, in the walls of which a large number of sheets of glass are inserted, but not puttied in. These boxes were divided into four divisions by means of partitions, so that the gases had to traverse them, entering at *A* and escaping at *B*. The bottom was inclined towards the two longer sides, in order to allow the condensed products to run off readily. These condensers, too, have been discontinued for the Exeli furnace, but have been retained for the furnaces which are treating ore fines.

At present the condensing plant consists of brick chambers and of cooled iron pipes. From the above-mentioned brick chambers the gases enter two systems of cooled iron pipes, and then again a series



FIGS. 285—287.

of brick chambers. From the last chamber they are conducted by a wooden box into a tower, and then through another wooden flue into a main flue common to a number of furnaces, through which they are drawn by a Guibal fan. The construction of the iron pipe condensers is shown in Fig. 288.<sup>1</sup> From the brick chambers connected with these condensers, the gases and vapours escape through three pipes made of wrought iron 0·18 inch thick, inclined at an angle of from 3° to 20°. They are 22 inches in diameter and 19 feet long. From these they pass into three corresponding systems of tubes, which have the shape shown in the figure, and which are contained in a wooden box 10 feet long, 10 feet deep, and 6 feet 9 inches broad. These pipes are made of cast-iron, and are surrounded by water, which enters the lower part of the box and escapes heated from the upper part. The pipes are 22 inches in diameter and 0·75 inch thick. The inclined pipe lying in the bottom

<sup>1</sup> Egleston, *op. cit.*

of the box serves to collect the products of condensation. From the lower end thereof these products, namely, mercury and soot, can be run off by means of a smaller pipe. They run first on to a plate, *p*, covered with indiarubber, upon which the soot is retained, and thence enter a vessel in which the mercury is collected, whilst the acid water runs out over its edge. The vertical as well as the inclined pipes terminate in blind flanges, which can be removed in order to clear out the soot. From the last vertical pipe, gas and vapour enter a brick chamber provided with movable partitions, and traverse it in the direction described above. By moving the partitions, which resemble dampers, the rate of the gas current can be regulated. The

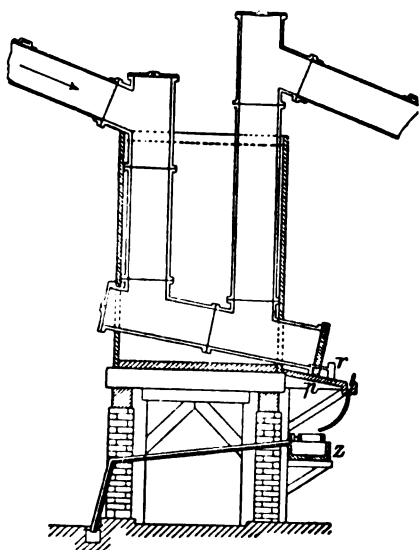
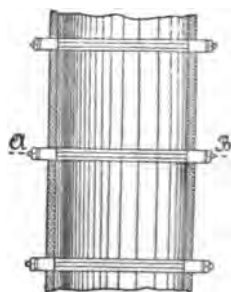
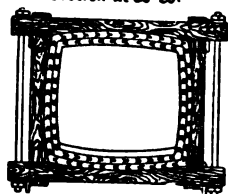


FIG. 288.



Section at A-B.



FIGS. 289 and 290.

wooden flues through which the gases are conveyed to the fan are shown in Figs. 289 and 290. They are built of two layers of curved planks, between which there is a coating of asphalt. Their inner surfaces are coated with a mixture of asphalt and coal-tar, and they are coated externally with asphalt. At every 6 feet they are supported by a wooden frame. The Guibal fan, which provides the draft for five furnaces, has an iron frame, the vanes being of wood. Its diameter is 9 feet, its width 28 inches. Those parts of the fan that are made of wrought-iron have to be renewed every two years. In working the furnace, it is first charged with ore containing from 5 to 8 per cent. of quicksilver, and sometimes as much as 10 per

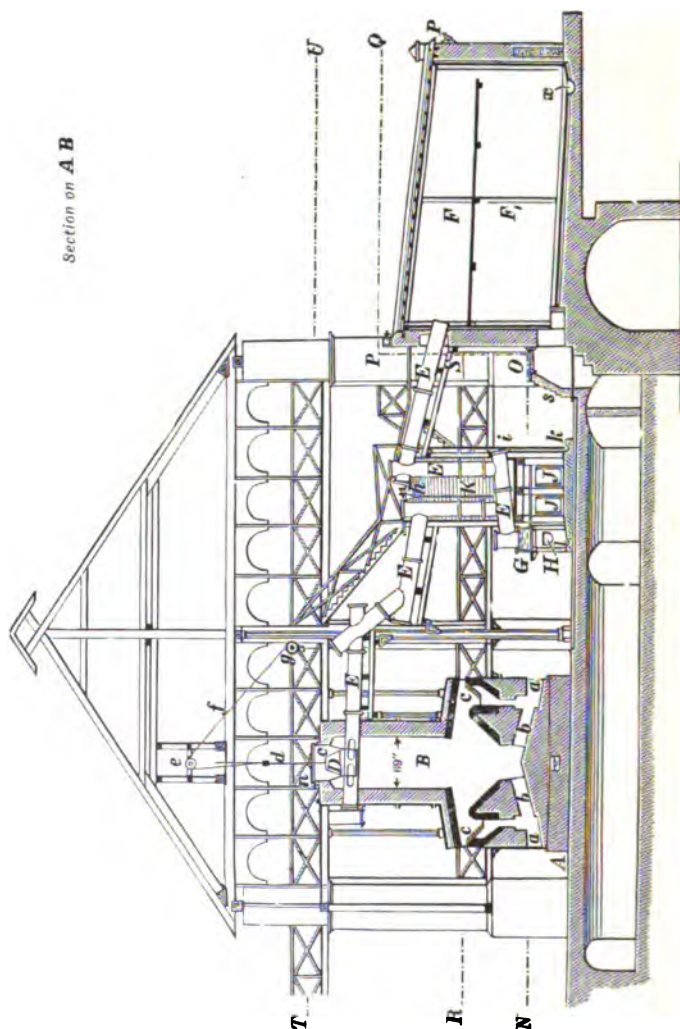


cent. The ores are mixed with  $1\frac{1}{2}$  per cent. of charcoal. The fuel burnt on the grates is fir wood or oak. When the furnace is in regular operation, it is charged and drawn every two hours; every charge remains about  $2\frac{1}{4}$  days in the furnace. A pair of furnaces are worked by two men on the shift, 10 tons of ore (*granza*) being treated in 24 hours, the furnace being capable of putting through a larger quantity of poorer ores. The consumption of fuel amounts to 85 cubic feet of cord wood per 24 hours. According to Egleston, in the year 1888 one of the two furnaces at New Almaden was in operation for 345 days, and treated 3,185 tons of *granza* ores. The product was 7,062 flasks, each containing 76.5 lb. of mercury, or a production of 8.48 per cent. A second furnace was only in operation 157 days, and treated 1,486 tons of ore, producing 3,050 flasks of mercury, or an output of 7.84 per cent.

### *The Langer Furnace*

This furnace was designed in 1878 by Langer in Idria, and is a modified Exeli furnace with an iron shell. It differs from the latter chiefly in being oval in horizontal section and in not standing by itself, four furnaces, built side by side, being enclosed in one common shell. The construction of such a block of four furnaces, together with the condensing arrangement, is shown in Figs. 291 to 293; *B* are the furnaces standing upon an iron plate surrounded by a shell of iron. The shafts for a distance of 14 feet from the throat have a cross section of 7 feet 6 inches by 5 feet 9 inches, and contract from this to the bottom of the furnace, a height of 9 feet, to a cross section of 5 feet 9 inches by 3 feet 8 inches. On either side of the furnace there are two step grates, making altogether four fireplaces, *c*. Beneath each of these are the four openings, *a*, *b*, through which the distillation residues can be drawn out. Charging is effected by lifting the cone, *D*, by means of the rod *d*, in the casing *C*. The upper end of the latter is closed by means of a cover, *n*, provided with a water seal, the cover being made of wood and balanced by means of the counterpoise, *p*. The gases and vapours escape through the upper part of the furnace into cast-iron tubes, *E*,  $18\frac{1}{2}$  inches in diameter in the clear, there being three of these tubes to each furnace, which are provided on either side with two oval openings, through which the gases and vapours enter the tubes. These tubes communicate with the condensing tubes proper, which are also made of cast-iron. There are three rows of these tubes for each furnace, surrounded by the cooling box, *K*, in which a constant current of cold water circulates to promote condensation in the same way as has

been explained on page 363. The cold water enters through the tube *h*, at the bottom of the box, the heated water running out at the upper part through the tube *i* and the gutter *k*, and thence into



the sump *m*. The products of condensation collect in the box *G*, from which the mercury, with a portion of soot, is run off into the reservoir *H*. The acid waters are run out of the soot collector *G* alternately into two soot tanks *I*, and after settlement are run off

through the gutter *k* into the sump *m*. The gases and uncondensed vapours pass into the condensing chambers *P*, which are built of brickwork pointed with cement. The walls are covered first with asphalt, then with a layer of cement, and finally with smoothly

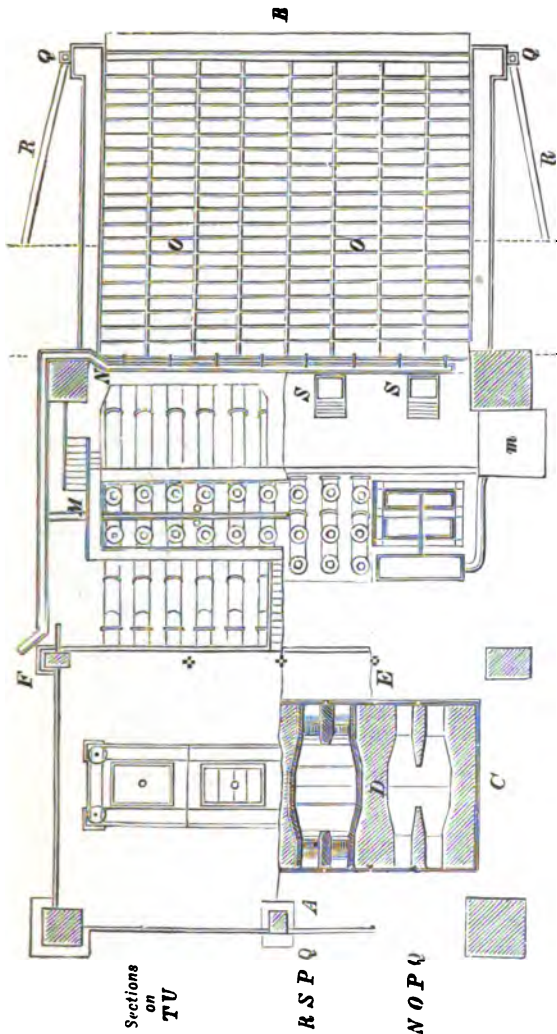


Fig. 292.

planed wood. The bottom of the chamber consists of a layer of concrete 3 inches thick, upon which there is a thick asphalt pavement. The cover of the chamber consists of the dished-out cast-iron plates *O*, which are bolted together, the joints being made with

rubber. This cover is cooled by means of a stream of water conducted over it. The chamber is divided by wooden partitions into four divisions corresponding to the four furnaces. Each of these divisions is divided by a horizontal partition into an upper chamber *F* and a lower one *F'*; from these chambers the gases pass through the flues *S* into a subterranean system of chambers, thence into a series of central chambers common to the whole furnace, and finally pass to the stack or fan. One of these furnaces used to put through in 24 hours 15.9 tons of lump ore containing 0.2 to 0.8 per cent. of

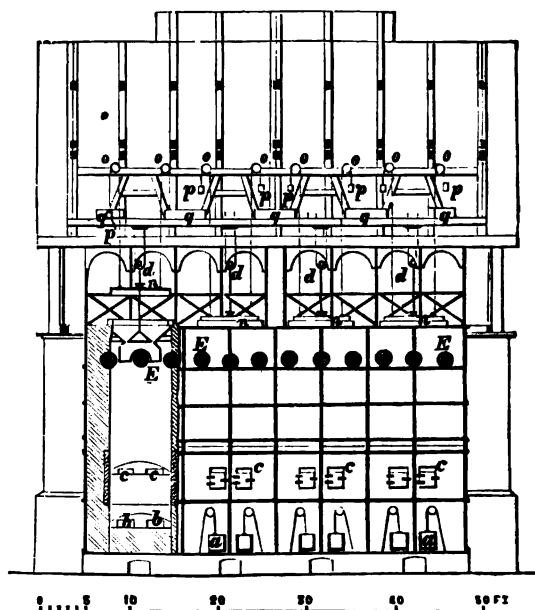


FIG. 298.

mercury, 24 cubic feet of wood being consumed to each 100 tons of ore. In 1893, the loss of mercury was 9.12 per cent. according to Exeli. The fireplaces of these Langer furnaces have at present been bricked up, and they are used as shaft furnaces proper, into which the ores are charged together with charcoal. The condensing arrangement has been replaced by Czermak condensers with stoneware pipes.

### *The Knox Furnace*

This furnace was erected in the years 1874 to 1875 at the Redington Mine, and was also introduced at a number of other

Californian works. It was intended to treat simultaneously lump ore and ore fines. Although it gave good results, both for lumps and for mixtures of lump and fine, provided the latter did not exceed a definite proportion, and showed itself especially far superior to the modified Idrian furnace, it has not come into general use, as was at first expected, in consequence of the construction of furnaces specially for the treatment of ore fines, and on account of the existence of other good furnaces suitable for the treatment of lump ores. At present it is probably out of use. Its special advantage was said to be that it would treat satisfactorily ores containing only  $1\frac{1}{2}$  per cent. of mercury, whereas in the modern furnaces used for the treatment of ore fines, ores with only 0.3 per cent. of mercury can

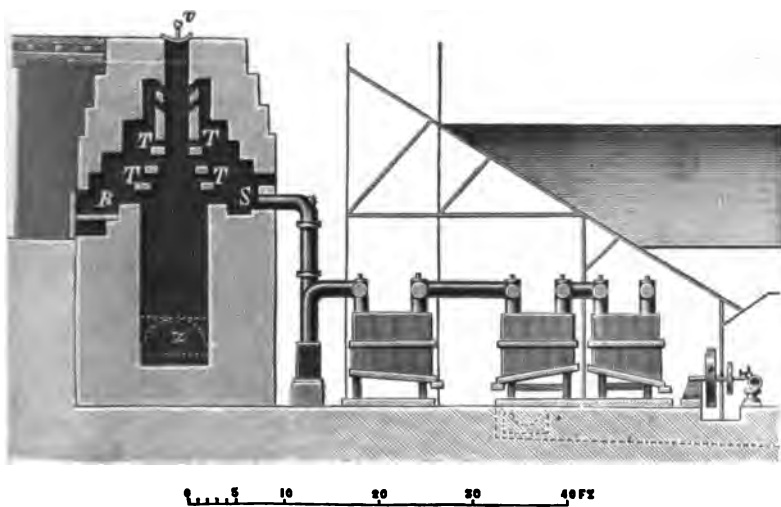


FIG. 294.

be profitably worked. Its construction is shown in Figs. 294 and 295. It consists of a brick shaft with walls widening upwards stepwise, and with a lateral fireplace in the middle of its height. The height of the furnace, of which two, or in case of need four, are best built side by side, amounts to 39 feet. The shaft is rectangular in horizontal section. As shown in the figures, the furnace widens from the throat to the fireplace, the latter lying 20 feet below the former. The shaft proper is, as is shown, 7 feet square. In order, however, to heat the ores thoroughly, the side containing the fireplace has been brought nearer the opposite side, to within 2 feet in the newer furnaces, according to Egleston.<sup>1</sup> At the level of the fireplace the

<sup>1</sup> *Op. cit.*, p. 842.

cross-section of the shaft therefore presents in these furnaces a rectangle of 7 feet by 2 feet. At the opening for the removal of the residues, the cross-section decreases again down to 2 feet by 2 feet. The arches *T* form two chambers, *R* and *S*, the former of which contains the fireplace, whilst the escape pipe for the gases and vapours lies in the second. The five arches *T*, of which the two top ones are smaller than the rest, are spaced some distance apart, leaving openings, through which the flames enter the shaft at one side, and escape at the opposite side into the chamber *S*. By means of this

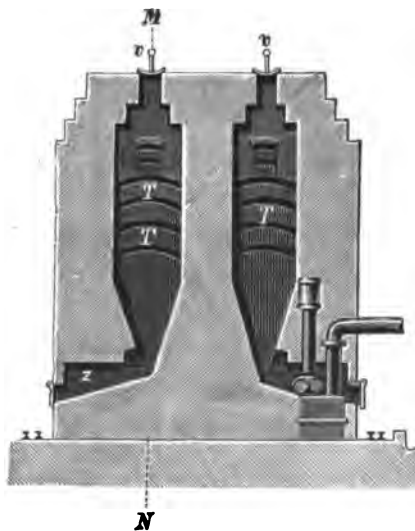


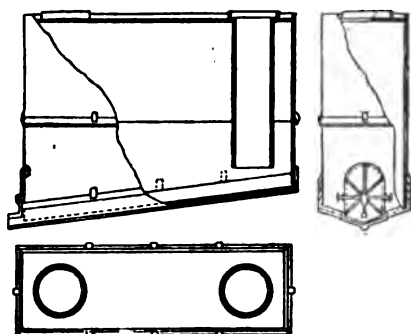
FIG. 295.

arrangement, the flames are forced to traverse the column in the shaft in a horizontal direction, and, together with the products of oxidation of the sulphur and the mercurial vapours, are drawn by means of a fan into the condensers. The three lowermost arches are stepped backwards, so that the shaft proper widens out at this point. Owing to this widening the column of ore is rendered loosest opposite the fireplace in order to promote a better circulation of the flame through the ore, and also to avoid any ore dropping through

the slots into the above-mentioned chambers.

The fire heats the ore to such a temperature that it will continue to burn by itself in the lower part of the shaft; *z* is the opening through which the residues of distillation are drawn out. The throat is closed by a cover *v* in the shape of a segment of a sphere, which is pushed to one side by means of a projection on the ore waggons. The bottom of the chamber *S* is covered with stout plates of iron which are to prevent the penetration of the mercury into the brick work. From this chamber the gases and vapours pass by means of a cast-iron pipe, 1 foot 6 inches in diameter, into Knox-Osborne condensers. These consist of a series of 16 to 19 boxes of cast-iron and wood, rectangular in horizontal section and with an inclined floor which are united by means of cast-iron elbow pipes. The construction is shown in Figs. 296 to 298; the boxes are 8 feet long, 2 feet 6 inches broad, 5 feet high at one end and 6 feet at the other. They

are cooled by allowing water to trickle first over the cover and then over the sides. The last eight boxes are made of wood. As the bottoms of the iron boxes are constantly covered by a layer of fluid, they are not more strongly attacked than the sides; in consequence of this observation, the thickness of the bottom plates, which was first very great, has been diminished. Attached to the last condensers is a Roots blower, one to each furnace, which draws the gases through a wooden flue into a wooden tower 15 feet high and 4 feet in section. This tower is filled with stones, over which water trickles, so as to condense the last particles of mercury. The uncondensed gases escape from the tower through a long flue to the summit of a hill, where they are allowed to escape into the open air. The products condensed in the boxes flow through an opening at the lower end of the inclined bottom plates into gutters, and thence into a pan, from which the mercury is ladled out, whilst the acid waters are run into settling tanks, in which any metallic particles carried by them are deposited. On account of the high temperature of the gases



FIGS. 296—298.

and vapours as they enter the condenser, the greater part of the mercury is deposited only in the middle boxes of the series, whilst relatively large quantities of acid waters are condensed in the last boxes. The ores are charged and the residues drawn at intervals of an hour. In normal working 1 ton is charged at a time, so that the furnace puts through 24 tons in 24 hours, the ore taking three days to pass through the furnace. At the Redington Mine the charge consisted, according to Egleston, of  $\frac{1}{2}$  to  $\frac{3}{4}$  of coarse ores and  $\frac{1}{2}$  to  $\frac{1}{4}$  of fines, the average quicksilver contents being  $1\frac{1}{2}$  per cent. When the larger quantities of fines were charged, or when the ores were damp, the furnace was unable to treat more than 12 tons per 24 hours. At the Redington Mine, when good wood was employed, its consumption amounted per 24 hours to 1 to  $1\frac{1}{2}$  cords per double furnace, according as the charge contained more or less fine ore. A single furnace treating 24 tons in 24 hours required six men during that time, a double furnace treating 48 tons eight men, and a block of four furnaces treating 100 tons 10 men. The removal of soot from the condensers

and tubes took place once a week; it only takes a few minutes for each of the boxes. On account of the powerful action of the fan, no gas or vapours can escape from the boxes during this process, so that the health of the men engaged in the operation is not impaired. There are no data as to the losses of mercury. As already stated, these Knox furnaces are now no longer built.

#### FURNACES FOR ORE FINES

##### *Hüttner and Scott Furnaces*

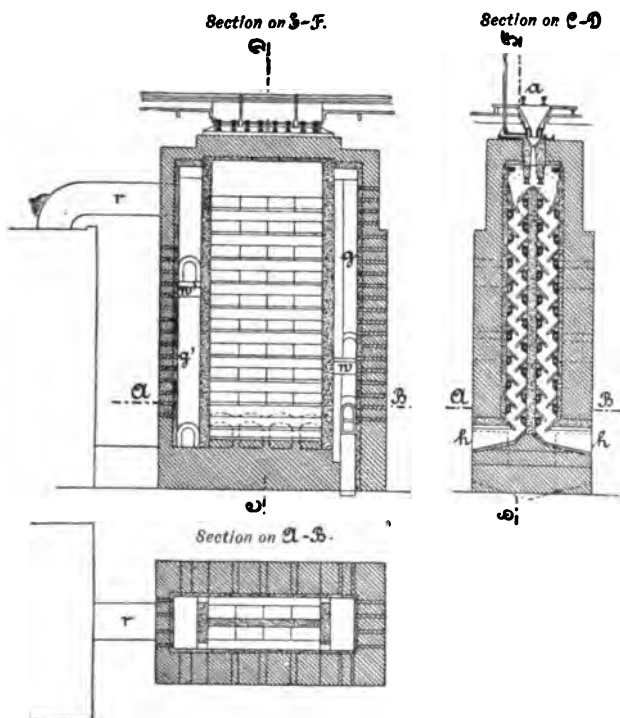
Hüttner and Scott have designed furnaces for the treatment of coarse-grained ores, known as *granzita*, of 3·2 to 1·2 inches cube, as also for the treatment of fine ore, known as *tierras*, less than 1·2 inches cube. These furnaces, which were first introduced at New Almaden in the year 1875, are shaft furnaces externally fired, in which the free fall of the ore through the shaft is prevented by means of inclined shelves, sloping at an angle of 45° in alternately opposite directions, upon which the fine ore (the angle of repose of which amounts to 33°) slips down, as in the case of the Hasenclever and Helbig furnace (Vol. I., p. 107). In these furnaces, however, the residues are not removed continuously as in the last-named furnace, but are drawn out from it at short intervals, either by hand or mechanically. These furnaces have given excellent results, and are largely used in California.

##### *The Granzita Furnace*

This furnace is distinguished from the *tierras* furnace principally by the interval between each pair of alternately inclined shelves being greater than in the case of the latter, amounting to 7 inches, and by the removal of the residues being performed without the aid of shaking appliances, as in the case of the *tierras* furnace. The capacity of the furnace depends upon the distance between the lower end of a shelf and the surface of the plate lying next beneath it. The older furnaces were built with two shafts, whilst the most recently built consist of four shafts in one block, with a common fireplace. The general construction of the two-shaft furnaces is shown in Figs. 299 to 301. Each shaft is fitted with shelves inclined alternately at angles of 45°. If all the shelves are charged and the withdrawing apertures are full of ore, then the ore cannot pass through the furnace, since the open spaces between the shelves are blocked with it. If this happens, then a channel is formed



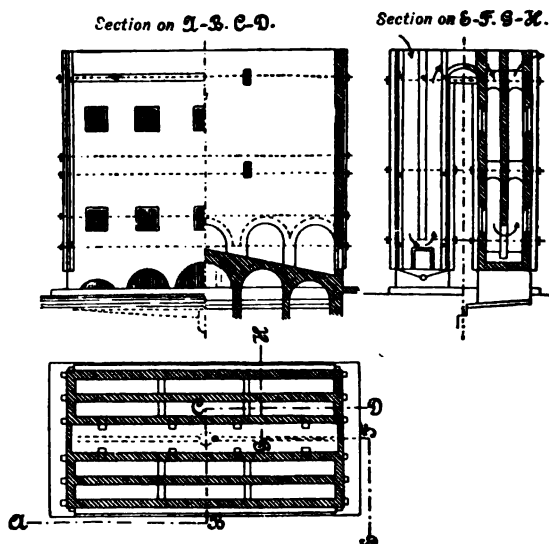
between the ore lying on one of the lower shelves, part of the side wall of the furnace, and the lower surface of the shelf lying next above. The gases from the grate along with air pass through this channel. As soon as the residues of distillation are drawn out through the apertures provided for that purpose, the ore lying above them slips down. The topmost shelves thus become free, and are then recharged with ore, the charging being performed by means of the hopper *a*. The flame and air pass in the opposite direction to



FIGS. 299—301.

the ore, and heat the shelves both below and above. The gases are compelled to travel this particular path by means of the partitions *w* and *w'*, made of fire-brick; from the grate lying beneath the partition *w* they enter the space *g'*, and then traverse the lowest third of the furnace longitudinally. Being prevented by *w'* from rising upwards in the chamber *g'*, they are compelled to traverse the second third of the furnace into the chamber *g*, and from it have to traverse the remaining third, entering the pipe *r*, which leads them into the condensing appliances. Each shaft is 27 feet 6 inches high, 2 feet

6 inches broad, and 11 feet 6 inches long. There are ten inclined tiles on either side of the shaft. The vertical chambers in which the above-named partitions are arranged are 2 feet 6 inches wide. The ore, which is charged by means of the hopper *a*, is passed through a sieve of 3.75 by 2.5 inches mesh. The hopper is closed at its lower end by means of a cone. The distillation residues are drawn out at intervals of 40 minutes in quantities of  $\frac{1}{2}$  ton each time for the two shafts, a similar quantity of ore being charged in the furnace at corresponding intervals. In 24 hours the two shafts together put through 18 tons of ore with a consumption of  $\frac{3}{4}$  cord of



FIGS. 302-304.

wood, three men being engaged on the furnace per shift. In 1888, this furnace was in operation for 128 days at New Almaden, and put through 2,375 tons of ore, producing 1239 flasks of mercury, equal to an output of 1.995 per cent.

The condensing appliances are chambers built partly of brickwork, partly of glass and wood. The condensers of glass and wood form the last chambers into which the gaseous current enters after it has been cooled. The construction of the brick condensers is shown in Figs. 302 to 304. They consist of chambers 27 feet high and 6 feet broad, divided by a brick partition into two divisions. The chambers are connected by means of brick flues 4 feet square; for the convenience of cleaning them out, there

are two rows of openings 2 feet square in the side walls. These are closed by iron plates in the hotter chambers, and by sliding windows in the cooler ones. The floor is coated with cement, on top of which there is a layer of asphalt in the cooler chambers. The floor is inclined towards the centre, as also towards one side. The walls of the cooler chambers are coated with a mixture of asphalt and coal-tar. The path of the gases and vapours through the chambers is indicated by arrows; they enter the upper part of the condenser, traverse the first division, enter the second division from below, traverse it and escape at its upper end into a second condenser, which they traverse in the same direction, pass through the following condensers, and finally reach the fan. The mercury is deposited upon the inclined floor of the chambers, and flows through a gutter in them into an external gutter made of brickwork and lined with asphalt from which it runs into the collecting pans. Quite recently the walls of these brick condensers have been provided with so-called water-backs, consisting of cast-iron boxes 43 inches long, 16 inches wide, and 14 inches deep, in which water circulates. They are provided with an external flange 8 inches broad, to which the cover lined with wood is bolted. There is a partition in them which forces the cold water, entering at the bottom by means of four pipes, to circulate. These water-backs are applied to the first two chambers; they have given good results, and compel by far the greater portion of the mercury to condense in the first brick chamber, whilst it used formerly to be deposited in the fourth to the seventh chambers. Their life is up to four years. Chambers provided with these water-backs are considered at Almaden to be the best of all condensing appliances, and have to a great extent replaced glass and wooden condensers.

The arrangement of the most modern type of condenser, made of glass and wood, of which there are 12 to 15 following the brick condensers, is shown in Figs. 305 to 307. They are connected with each other alternately above and below, and consist of towers 25 feet high and 4 feet square. They are built of glass plates let into



*Arrangement  
of the floor*



FIGS. 305-307.

wooden frames and contain no iron whatever. The floor consists of plates of glass lapping one over the other like the slates of a roof, and it inclines towards the side, at which there is a gutter for the removal of the mercury. This gutter terminates in an earthenware pot for the collection of the mercury. The roof, and the flues uniting the towers are also built of glass. The gases and vapours are forced to alternately rise and descend in these condensers. Very little mercury, but a great deal of acid water, is deposited in these condensers, the temperature of which varies from  $55^{\circ}$  to  $80^{\circ}$  Fahr. In order that these condensers may remain tight, they must be kept in continuous action, otherwise the wood shrinks for want of moisture. From the glass chambers the gases pass through a wooden flue of the construction described on page 364 into a tower of brickwork, from which they are drawn off by a Guibal fan and forced into a stack.

The arrangement of a Granzita Furnace<sup>1</sup> with four shafts is shown in Figs. 308 to 310, which represent a double furnace of the above kind. Fig. 308 shows an elevation and a vertical section on  $ZZ$ ; Fig. 309 a vertical section on  $OPQR$ ; Fig. 310 a horizontal section on  $VWXY$ . The entire furnace is 36 feet high, 25 feet 6 inches long and 17 feet 6 inches broad. The floor of the furnace is rendered impervious to quicksilver by means of cast-iron plates  $a$ . There are four shafts in the furnace, with one fireplace common to all. The dimensions of each shaft are 27 feet high, 11 feet 6 inches wide and 26 inches deep. The tiles upon which the ore slips down are inclined at an angle of  $45^{\circ}$ , the distance between two tiles inclined in opposite directions amounting to 8 inches.  $J, J$  is the grate burning wood as fuel, and fired from two opposite sides. The air required for combustion is supplied by means of the pipe  $g$ , which traverses a portion of the condensing chambers, and is thereby heated; it enters by means of a number of small flues under the grate. The flame passes in the same direction as it does in the Granzita furnace with two shafts. At the two narrow sides of the shaft there are chambers, III and IV, with their partitions  $m$  and  $n$ . The flame passes from the grate  $J, J$  in the lower part of chamber III up to the partition  $m$  in this chamber, and then passes through the openings  $X$  into the lower third of the four shafts, which it traverses lengthwise, escaping through the openings  $XI$  into the chamber IV. In this chamber there is a partition,  $n$ , at two-thirds of its height, which forces the gases and vapours to traverse the second third of the four shafts lengthwise, entering the chamber III through

<sup>1</sup> Egleston, *op. cit.*, p. 877; *Eng. Min. Journ.*, 1885, p. 174.

the openings *XI*. From the latter chamber they enter the last third of the four shafts, traverse it, and pass into the upper portion of

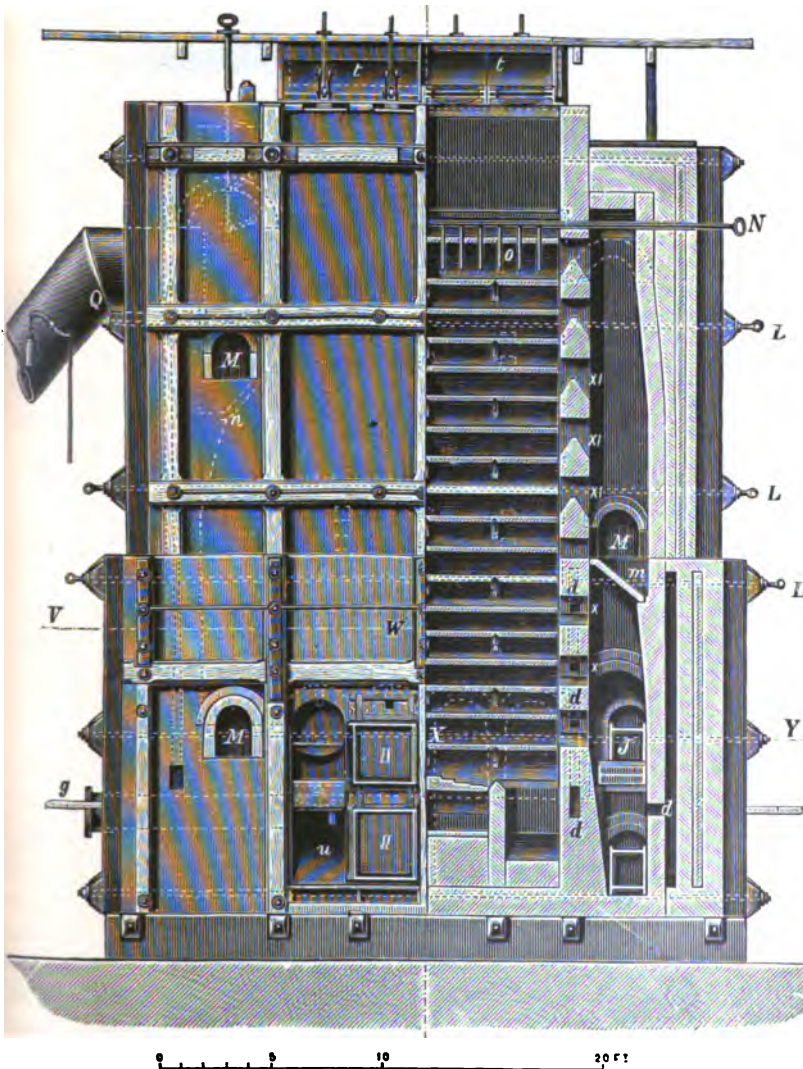


FIG. 308.

the chamber *IV*, from which they are conveyed by the cast-iron pipe *Q* into the condensers. The openings *XI* have an inclined floor, so that any soot collected in them can slide down, the object

being to prevent the openings becoming stopped up either partially or entirely. In order to keep all the openings clear, and to prevent the

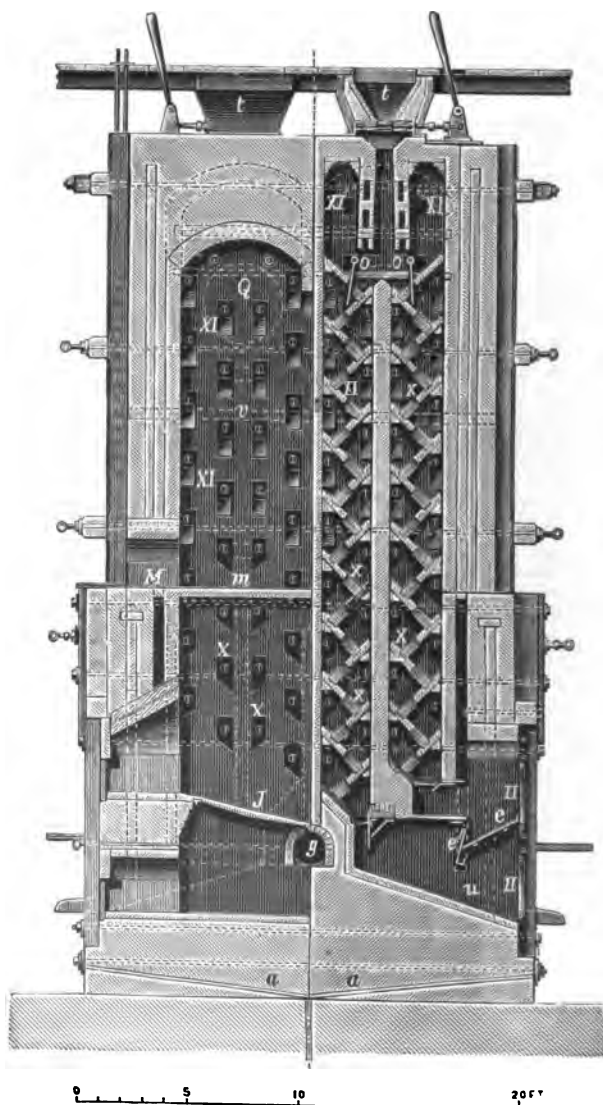


FIG. 309.

ore settling upon and between the inclined tiles, as is apt to happen in the case of wet ores, gas pipes 3 inches in diameter are built into the wall of the furnace opposite each partition. These pipes are

kept closed during the operation by means of clay plugs, and through them iron bars *L* can be introduced, by means of which any flue-dust can be removed through the doors *M*. Any ore that has fritted on to the topmost tiles can be removed by means of the iron rables *O*, which are attached to the sliding bar *N*; *t* are the charging hoppers, the lower portion of which is closed by means of slides controlled by a lever; *u* are openings that can be closed by

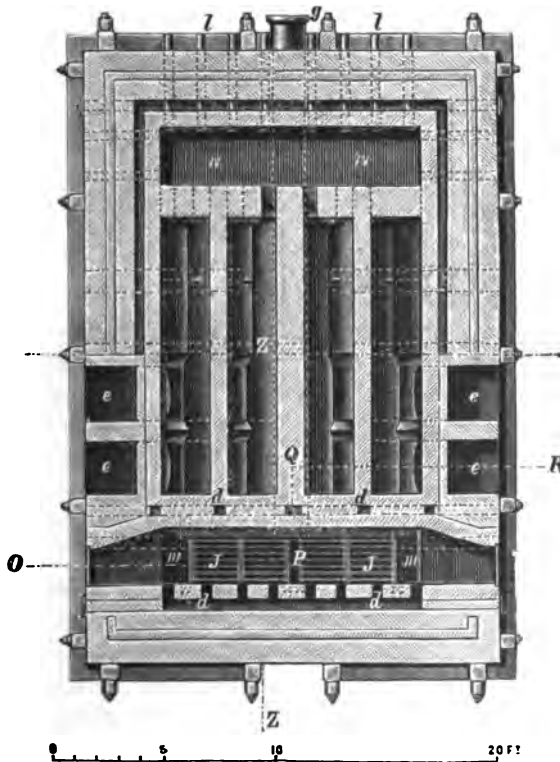


FIG. 310.

means of doors, through which the residues of distillation can be removed from the furnace. There are four such openings on either of the longer sides of the furnace. The distillation residues from the inner shafts fall direct upon the inclined floor of the furnace which is covered with cast-iron plates. The distillation residues from the outer shafts fall upon the plate *c*, and can only drop on to the bottom of the furnace after the slide *e* is drawn back. These residues are drawn out from each side of the furnace

at intervals of forty minutes, one-eighth ton being removed from each of the eight openings, so that 2 tons altogether are removed from the furnace every 80 minutes, a corresponding quantity of fresh ore being charged at equal intervals. The ore remains for 30 hours in the furnace, the quantity of ore put through in 24 hours amounting to 36 tons, during which time the furnace consumes from  $1\frac{1}{2}$  to  $1\frac{3}{4}$  cords of oak wood. Five men work a furnace in a shift when it alone is in operation. If the above described 2-shaft furnace works at the same time, 3 men are sufficient. The percentage of mercury contained in the ores treated in this furnace is often as low as  $\frac{3}{4}$  to 1 per cent. In the year 1888, this furnace was in operation 236 days, and treated 8,420 tons of ore, from which 3,073 flasks of quicksilver ( $54\frac{1}{2}$  lbs.) were obtained, equal to 1.395 per cent. of mercury. This furnace is to be preferred to the 2-shaft furnace, as may be inferred from the fact that the costs of treating a ton of ore amounted to \$0.64, whilst in the 2-shaft furnace they amounted to \$1. In the former furnace wages amounted to \$0.28, in the latter furnace to \$0.46.<sup>1</sup>

The condensing arrangements consist of brick chambers and chambers of glass and wood as in the 2-shaft furnaces. The two first brick chambers and the fourth chamber are fitted with cast-iron water-backs let into the sides as already described. The third chamber contains drying kilns for the fine ore, which promotes the cooling of the gases and vapours. There are two water-backs in each of the brick chambers, there being ten of these altogether, followed by fifteen condensers of glass and wood. From the latter the gases escape into a brick tower and are finally conveyed by a flue to the Guibal fan, which forces them into a stack. A more recent furnace with four shafts and condensers to correspond, which is capable of putting through 50 tons of ore averaging 1 per cent. of mercury in 24 hours, and which was constructed by Newcomb, at Oathill, California, as the outcome of many years' experience, is shown in Figs. 311 to 314.<sup>2</sup> Fig. 311 represents the plan; Fig. 312 the section on *AB*, and Fig. 313 the section on *CD* in Fig. 311, the latter giving also a side view of the condensing chambers; Fig. 314 the horizontal section on *EF* in Fig. 313. The ore is sifted on a grate at the mine into lump ore and fines, above and below  $1\frac{1}{2}$  inches in size, respectively. The lump ore is crushed in stone breakers down to  $1\frac{1}{2}$  inches. The fines from the mine and the stone breakers are charged into the hopper *A*, whence they pass through 8 doors *t* on to the drying plates *T*, which lie

<sup>1</sup> Eggleston, *op. cit.*, pp. 873, 879.

<sup>2</sup> *The Min. Ind.*, 1899, p. 582.



over the first condensing chamber (Fig. 312). The drying space is 25 square feet in area and slopes at  $30^\circ$ , and the ore is distributed uniformly over it by workmen who stand on the four steps *Z* (Fig. 312). The dried ore is withdrawn at the lower end of the plates through the doors *t'* into the gutter *X*, whence it is filled into waggons and run to the furnace charging hopper *M*. The hopper has at its lower end two slits *s*, corresponding in size and position to the whole length of the furnace shaft, and capable of being opened or closed by slides. The ore is fed into the furnace at intervals of an hour, the charge being 2 tons. The furnace is built of brick, has no iron casing, and is 22 feet long, 16 feet wide, and 37 feet high. The

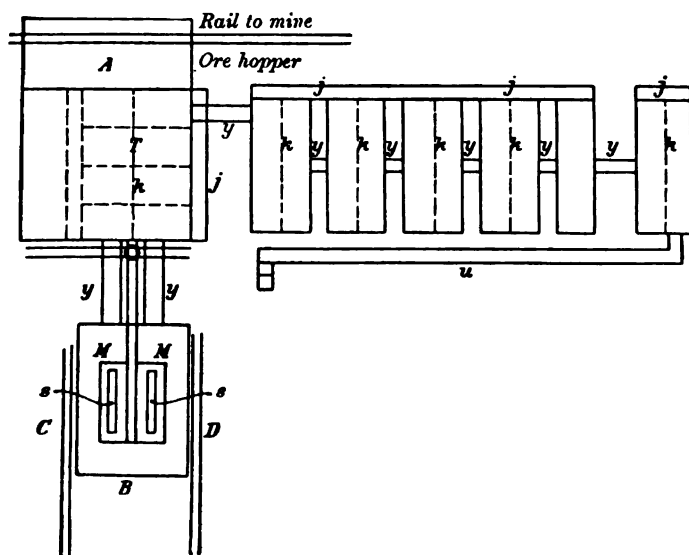


FIG. 311.

grate *a* (Figs. 312 and 314) stretches from one long side of the furnace to the other, and is fired at both ends. Wood is used as fuel,  $2\frac{1}{2}$  cords being consumed in 24 hours: *ii* are the four shafts (Fig. 314). The inclined shelves down which the ore slips are 9 feet long, and each comprises three plates of fire-clay, 3 feet long, 13 inches wide, and 3 inches thick, the total number of shelves in each of the four shafts being 24. The distillation residues are withdrawn from the ridge-shaped floor of the furnace through the doors *ff* (Figs. 312 and 313), whence they are taken in waggons to the spoil heap.

As the lowest point of the discharging openings is 5 feet below

the grate, the residues are cool enough by the time they are ready for drawing. This takes place every 15 minutes. The furnace puts through 50 tons of ore in 2,000 lb. charges every 24 hours; the furnace holds 40 tons, so that the ore remains in the furnace 20 hours. At the shorter ends of the 4 shafts are chambers, *a* and *c* at one end, *b* and *d* at the other, each chamber being separated from its neighbour by a fire-proof slide *n*, and each connected to the shafts proper by the openings *w*, 7 inches high and  $4\frac{1}{2}$  inches wide. One of the openings is under each inclined shelf, and is closed to the passage of ore by the ore itself, provided that this is not set in motion by the with-

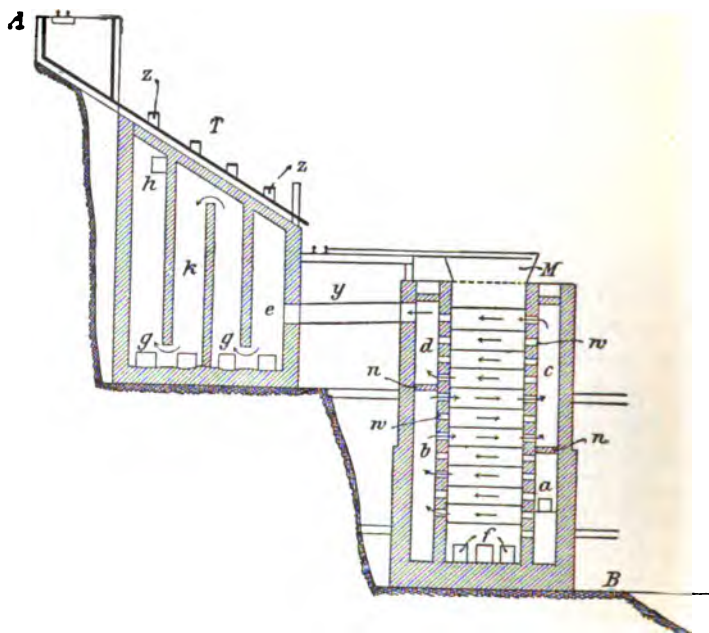
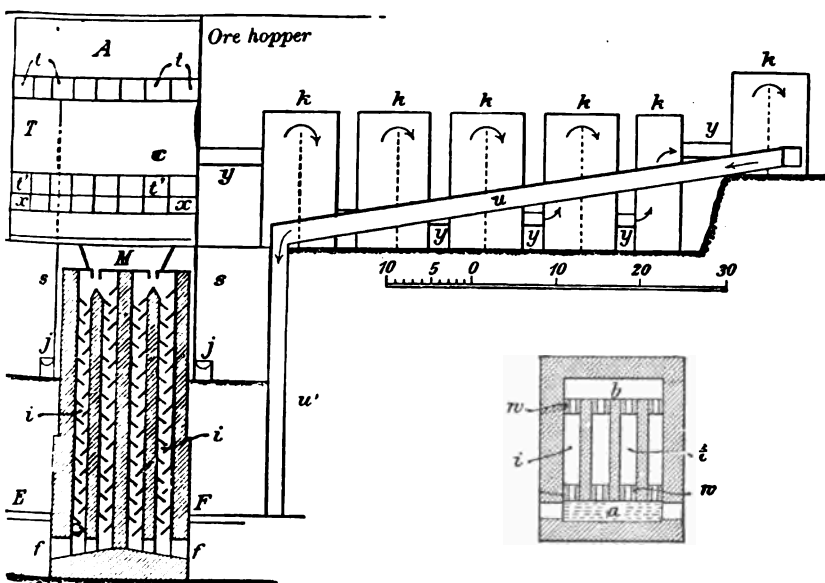


FIG. 312.

drawal of the residues. Channels for the passage of quicksilver vapour, air, and other gases are formed by the upper surface of the ore, the lower surface of the shelf next above and the side wall of the furnace, and the openings *w* at the shorter end of these passages allow of the escape or entry of the gases and vapours. The gases and hot air from the grate and the chamber *a*, pass through these openings *w* into the four shafts and along these channels, escaping at the end of these through corresponding openings in the lower half of the chamber *b*, thence through the openings *w* into the upper half of this chamber, and in like manner into the lower half of chamber *c*.

the upper half of the same chamber, and the chamber *d*, escaping eventually from this through the pipes *y* into the first condenser. The path of the vapours through the shafts is shown by arrows in Fig. 312. The furnace is kept at a cherry-red heat. Corresponding to the openings for the passage of vapours, there are holes in the outer wall of the furnace which serve as peep-holes and for the introduction of tools.

In passing through the furnace the ore loses 10 per cent. in weight; the fuel consumption is 1 cord of wood per 40 tons of ore, and somewhat less than this for pyritic ores. The gases and vapours



FIGS. 313 and 314.

escaping from the chamber *d* pass through 2 cast-iron pipes 12 feet long and 2 feet 6 inches diameter, into the first condensing chamber *k*, and then through five similar chambers into the discharge flue which is connected with the exhausting appliances. The chambers are made of brick and are partitioned off by walls (shown by the dotted lines in Figs. 311 and 313) into 2 compartments. The fifth chamber, however, is not so divided, owing to its size and position. The path taken by the vapours through these is shown in Fig. 312. The chambers are connected with one another by cast-iron pipes *y*, and the gases escape from the last chamber through a sloping wooden flue *u* (Fig. 313), 60 feet long and 2 feet 6 inches by 2 feet in cross

section, into a vertical flue of the same section and 40 feet long. A fan at the end of this drives them into the open through a chimney 20 feet high. Each condenser, save the fifth, has a capacity of 12,400 cubic feet and a cooling surface of 12,000 square feet. The floors of the condensers are slightly concave and slope towards the openings *gg* (Fig. 312) for running off the quicksilver. Each compartment contains one such opening in the form of a light sliding iron plate, luted with clay. The quicksilver is run from these openings once a week into the pots *jj* (Figs. 311 and 313). The first chamber yields the largest amount of the metal, the last two but little. The exhaust steam from the machine which works the fan is blown into the first condenser where it is supposed to materially assist the condensation. A large amount of soot containing up to 30 per cent. of the total output of mercury, is removed from the condensers along with the metal itself, and the loss of mercury is given as 5 per cent. Four men per shift are needed for each furnace, two for drying and charging the ore and stoking the boiler of the fan-engine, and two for firing the furnace and withdrawing the residues. In a second furnace at these works the distance between the inclined ore-shelves is 3 feet 4 inches.

#### *The Tierras Furnaces.*

These furnaces are similar in construction to the Granzita furnaces, except that the interspaces between the inclined tiles are smaller, amounting to from 3 to 5 inches, whilst the distillation residues are withdrawn by means of so-called shaking tables of cast-iron. Some furnace blocks have been built with 2 rows of 2 and others with 2 rows of 3 shafts; the construction of the blocks containing 3 shafts in the row is shown in Figs. 315 and 316. The fireplaces and the arrangements for deflecting the flames are the same as in the Granzita furnace. The whole furnace is jacketed with iron. The interspaces between the tiles of the outer shafts are 5 inches wide, those of the inner shaft 3 inches. It was thought that ores of rather coarse grain (Granzita) could be worked in the outer shaft. Nevertheless it was found that the heat which was quite sufficient for tierras, was not high enough for the coarser ore, so that the furnace is only treating tierras at present. Each shaft is 31 feet high, 23 inches broad, and 9 feet long. The grate is 5 feet above the discharging openings, these being protected by cast-iron plates: their width is 3 or 5 inches, and they extend over the total length of the furnace. There is one common discharging opening for every 2 shafts. Below them are the cast-iron shaking tables, which are

carried upon wheels running upon rails. When these tables are immediately below the discharging openings they support the distillation residues that drop upon them until the natural angle of repose is reached. As soon, however, as the tables are pushed backwards and forwards by means of levers, the residues slide into a vagon running beneath them. The residues are thus removed every 10 to 15 minutes, a ton being withdrawn from every pair of shafts in 2 hours, and an equal quantity of fresh ore charged.

The total quantity of ore, which all the 6 shafts of the furnace are capable of putting through in 24 hours, amounts to 36 tons,  $2\frac{1}{2}$  cords

*Section on A-B.*

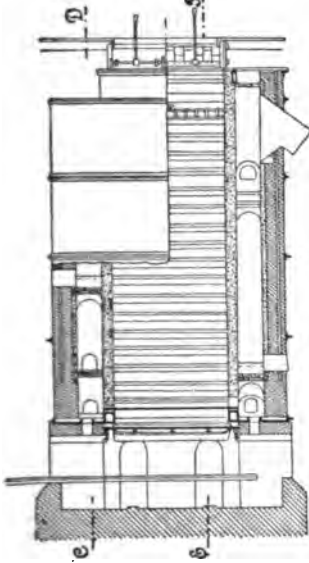


FIG. 815.

*Section on C-D. Section on E-F.*

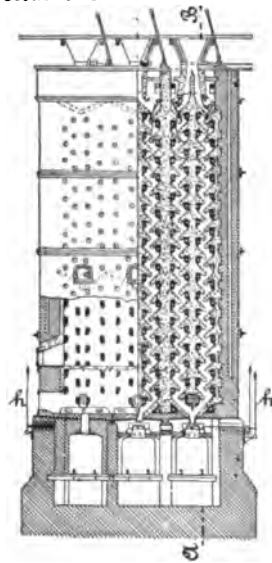


FIG. 816.

wood being used during that time. The ore remains about 34 hours in the furnace. There are three men on the shift. In the year 1888 this furnace was in operation for 255 days, treated 9,111 tons of tierras and produced 3,078 flasks of mercury, equal to an output of 1.29 per cent. The cost of treatment of a ton of ore amounted to \$0.72, half of which was for labour and half for fuel.

The double furnace with 2 pairs of shafts put through 24 tons in 4 hours with 2 men on the shift. At first the cost of treatment per ton of ore amounted to \$1.73, but later was reduced to only one-half that amount. In the year 1888 this furnace worked for 200

days, treated 4,737 tons of tierras, and produced 1,686 flasks of mercury, equal to 1.36 per cent. Nothing is said with regard to the loss of mercury.

The mercury is condensed in brick chambers, some of which are fitted with water backs. A portion of the hot gases and vapours surrounds a drying kiln for the damp smalls and is afterwards introduced into condensing chambers. These shelf drying kilns are fitted with inclined tiles like the Tierras and Granzita furnaces. They are fully described in Egleston's work, Vol. II., page 871.

### *The Livermore Furnace*

This furnace was introduced by C. E. Livermore at the Redington Mine, Knoxville, California. It consists of a row of narrow channels lying side by side and inclined at  $50^\circ$ , in which the flame ascends, whilst the ore, the descent of which is repeatedly interrupted, slides down upon the floor of the channels, dropping at last into a cooling chamber. The principle upon which the construction of the furnace depends is that of the older zinc blende calcining furnaces of Hasenclever. The construction of the furnace is shown in Fig. 317. *S* is one of the inclined channels, the length of which varies from 30 to 35 feet according to the nature of the ore; the width is  $6\frac{1}{2}$  inches, and the height from the floor to the crown of the arch 12 inches. There are 11 to 20 of these channels side by side, and they are heated by means of the grate *R*, which is common to 10 or 11 of them. In the channels there are numerous projections, *r*, built of fire-brick and made roof-shaped, running across the channels, their object being to prevent the ore from sliding down too quickly. These project  $5\frac{1}{2}$  inches above the floor, and are 12 inches apart from each other. In the arch of the channels there are also projections built of fire-brick 4 inches in depth, placed half-way between each pair of projections from the floor, their object being to prevent the flame from following straight along the arch, and to force it down upon the ores. The fire grates *R* are 24 inches high and 26 inches broad; their length depends upon the number of channels lying side by side. Several fireplaces are required for a large number, whilst one fireplace fired from both sides suffices for 10 to 11 channels. The firebridge is 20 inches above the grate, and its top edge is 18 inches below the crown of the arch of the channel. The ore is charged through the hopper *w*, the lower end of which is 2 inches square. If it should become stopped up, it is cleared by means of iron bars introduced into the hopper. The distillation

residues pass at the lower end of the channels through flues *u* into the cooling chamber *B*, in which they are allowed to cool for awhile, and are then removed in waggons; the cooling chamber is connected with a condenser *T* by means of flues which collect any vapours escaping from the hot residues. *P* is an auxiliary fireplace for heating the floor of the channels. It has, however, been found

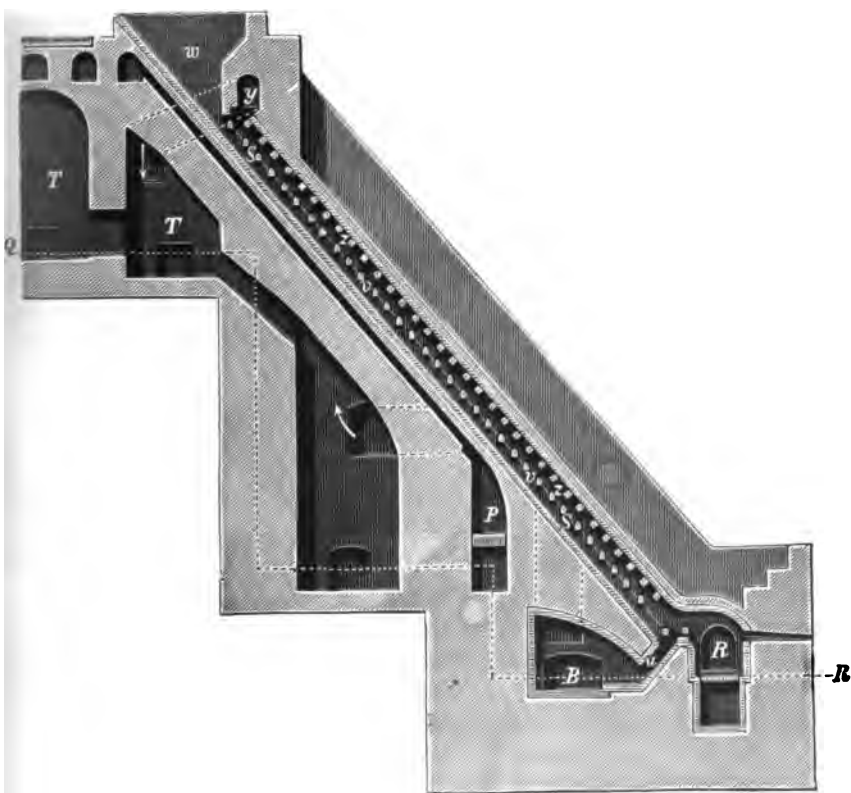


FIG. 317.

unnecessary, and it has been omitted in the more modern furnaces. The roofs of all the channels are covered with ashes in order to keep the heat together. There are sight-holes in the lower portion of the shafts in order to enable the process to be watched.

The vapours and gases escape from the flues *y* into the condenser, which consists of 5 brick chambers, *T*, 10 feet 9 inches high, 15 feet long and 4 feet wide, followed by 10 Knox-Osborne condensers, which have been described on page 370, and finally by 5 wooden

chambers with inclined floors, 8 feet in height, 20 feet in width, 6 feet high at one side and 5 feet at the other. Finally the gases pass through a long system of flues into a stack.

In a furnace composed of 10 to 12 flues,  $1\frac{1}{2}$  tons of ore are treated per flue in 24 hours, so that the whole furnace treats from  $17\frac{1}{2}$  to 24 tons; in the larger furnaces each flue will put through 1 ton in 24 hours. The consumption of fuel in a furnace with 10 to 12 flues is from  $1\frac{1}{2}$  to 2 cords of wood per 24 hours. Such a furnace is worked by 6 men in two 12-hour shifts.

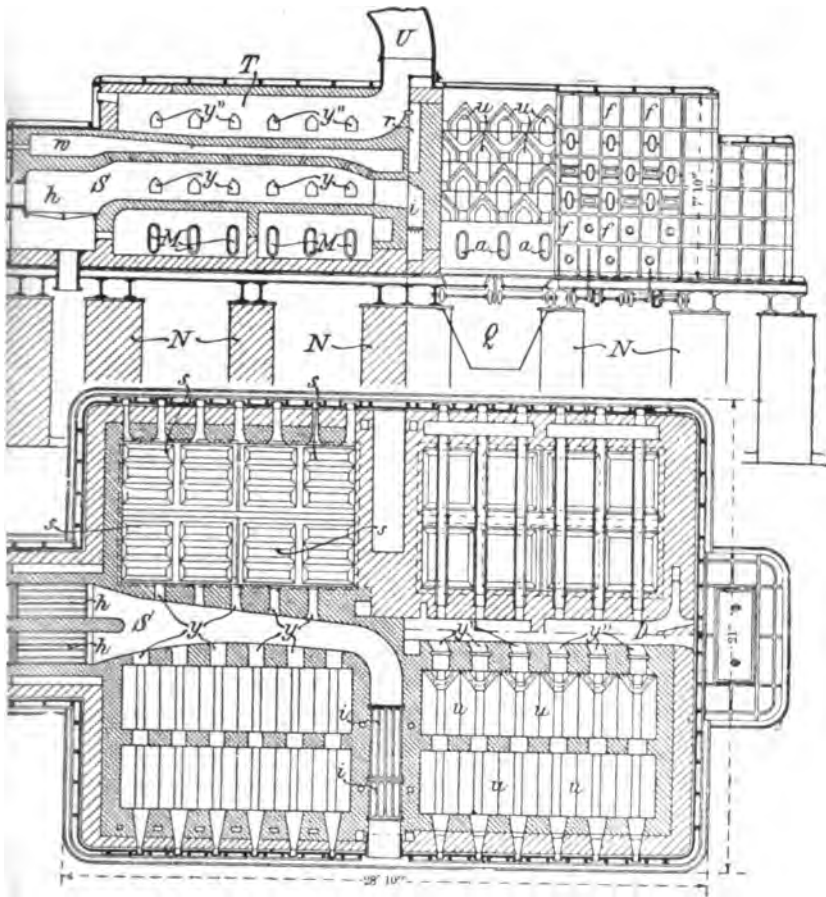
At the Sunderland Mine there is a Livermore furnace with 12 flues, which treats 15 to 16 tons of ore in 24 hours. The condensing appliances there consist of wrought-iron tubes 18 inches in diameter. At the Redington Mine there are furnaces with 16 to 20 flues respectively, the latter putting through 30 tons of ore in 24 hours.

#### *The Czermak Furnace (Schüttöfen).*

This furnace was introduced in 1886 by Czermak and Spirek into Idria, and has given very satisfactory results. It is far superior to the long-bedded calciners, in which a portion of the fine ore is calcined at Idria. The furnace consists of a shaft furnace with an iron shell; inside the shaft there are several rows of ridges made of fire-brick, the topmost row alone being of cast-iron, upon which the ore slides down. This arrangement somewhat resembles the Gerstenhöfer calciner, the differences being that in the latter the ore bearers are ridge-shaped below and flat above, the hot gases rise directly upwards, and the ore falls continuously from bearer to bearer, whilst in the Czermak furnace (as in that of Hüntner and Scott) the gases take a winding course upwards, passing through many horizontal channels, and the ore is shaken down periodically. The air required both for the complete combustion of the fuel, as also that required for oxidation, is heated. Four furnaces are combined to form a block. In the most modern furnaces there are 5 rows of 6 ridges each, of which the 4 lowermost rows are built of fire-brick, whilst the upper one consists of cast-iron. The construction of a furnace with only 4 rows of ridges is shown in Figs. 318 and 319. In the former *u*, *u* are the ridges lying one beneath the other. They are so disposed that the ore charged upon the topmost row of ridges slides gradually down their inclined faces, and reaches the bottom of the furnace free from mercury. The firing is done by means of the grates *h*, *i*, of which *h* is the main grate, *i* an auxiliary one. The flames from both fireplaces unite in the flue *S*. The air required for



the combustion of the fuel, as also for the oxidation of the sulphide of mercury, is heated both in the elliptical cast-iron pipes *a*, and in the lateral air chambers *r*. From the pipes *a* the air passes into the air chamber *M*, and from the latter, by means of vertical openings in its roof, into the flue *S*, in which the gases evolved from the fuel



FIGS. 318 and 319.

re completely burnt. Above the shaft *S* there is a second air hamber *w*, into which air passes both from the chamber *r* and through the openings *g*. The air contained in this chamber enters the flue through openings in the floor of the chamber; from that flue the products of combustion with the excess of air enter the furnace through the openings *y*, *y*. Below these openings there is a tier of

smaller openings not shown in the figures, through which the flames pass beneath the lowermost row of ridges. They rise at the opposite end, traverse the space under the second row of ridges, pass up under the third row, then the fourth, and finally escape laterally through the openings  $y''$ , which correspond to the spaces beneath the topmost row of ridges, whence they pass into the flue  $T$ , which carries all the gases and vapours evolved from the furnace through the pipe  $U$  to the condenser. The fine ore falling down in the furnace finally drops through the slots  $s, s$ , in the floor of the furnace. These slots can be closed or opened by a slide; when closed no ore can pass through the furnace, for the ore blocks up the spaces between the ridges, forming thereby a system of channels along which the vapours pass. The cross section of these channels is shown in Fig. 320,<sup>1</sup> where  $A$

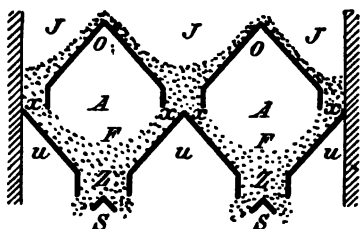


FIG. 320.

represents the channel formed by an upper ridge, by the ore which blocks the space  $x$  between the under side of this ridge and the two lower ridges  $u$ , and by the ore resting on the neighbouring halves of the two lower ridges and on the apex  $S$  of the ridge below these. The ore in the lower half of these channels comes in direct contact

with the hot gases, and the whole mass is heated by radiation and conduction. If the slots in the floor of the furnace be now opened, the ore falls into the sheet-iron hopper  $Q$ , and thence into the spaces between the columns  $N$ , and a corresponding quantity slides down through the furnace. When this happens the particles of ore become so mixed together in the troughs  $J$  (Fig. 320), and especially in the necks  $Z$  that there is no chance of any escaping the action of the flame and the oxidation by air. The height of the ore layer and the capacity of the furnace depend upon the distance between the lowest edge of a ridge and the sloping tiles of the next lower-lying ridges. The whole furnace stands upon a dish made of riveted sheet-iron which is supported by means of cement pillars protected with cast-iron plates. These pillars are let into the floor, which is carefully cemented, and in which there are cast-iron tanks, so that any escape of mercury is at once perceived. The residues are drawn out, and fresh ore is charged at intervals of two hours.

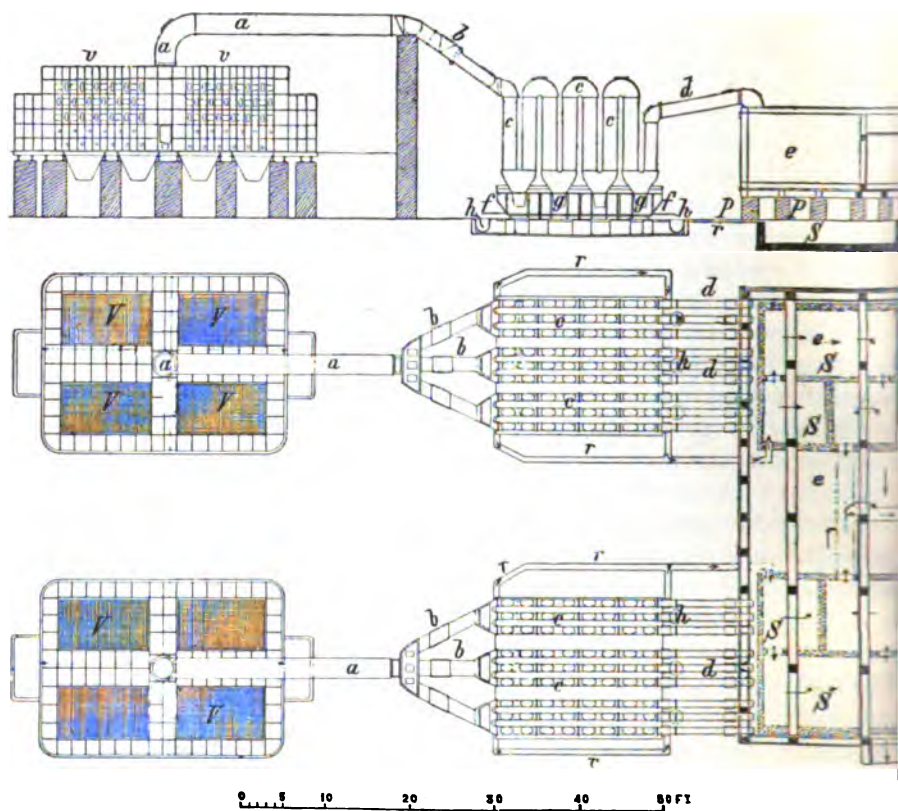
The condensing appliances consist of vertical pipes elliptical

<sup>1</sup> Spirek, *L'Industria del Mercurio in Italia. Conferenza tenuta in Torino al Congresso Nazionale di Chimica Applicata*. Torino, September, 1902, p. 7.

in cross section, made of stoneware, and cooled by means of water, followed by dust chambers. The condensers were first introduced by Czermak in 1878. The pipes were of cast-iron, and the stoneware tubes  $\frac{1}{4}$ -inch thick. The individual portions of the system of tubes are connected by means of cement, the whole system being supported by a wooden frame. The bottom-most ends of the pipes dip for 2 inches into boxes made of iron and lined inside with cement, and filled with water, in which the condensed mercury and soot collect. A furnace with four shafts is connected to nine rows of tubes with eight vertical tubes in each. These rows of tubes open into dust chambers built of 2-inch boards, which are made tight by grooves and tongues, and cemented with a cement made of quicklime and linseed oil. The dust chambers are supported upon brick pillars, their floor being protected by a layer of Portland cement 2.4 to 3.2 inches deep. The space below the chambers forms a sump for the escaping condensed water and for the wash water. The ground about the condensers is concreted, channels being made in the concrete, through which the condensed water and wash water can run into the sumps, which are also built of concrete. The construction of the condensers for a block consisting of 4 furnaces, the mode of connecting it with the furnace and with the dust chambers, as also the construction of the latter, is shown in Figs. 321 and 322. The gases and vapours from the four separate furnaces *V* collect in the gas-main *a*, and pass from it into three branch pipes *b*, through which they enter the condensers *c*. Below the latter are the boxes *f*, filled with water into which the ends *g* of the Y-shaped pipes dip. Through these boxes mercury flows off into the cast-iron pans *h*; the gases and vapours pass from the condensers *d* into the dust chambers *e*, which are provided with partition walls, and from the latter into the so-called central chambers. Below the dust chambers there are brick sumps *S*, into which the condensed water and wash water flow through the gutters *r*. *P* are the brick pillars which carry the dust chambers. Fig. 321 shows the combination of 2 blocks of furnaces with the condensers and the dust chambers. The cleaning out of the condensers, that is to say, the removal of the mercury from the stoneware pipes into the iron boxes, is undertaken every fifth day, when rich ores are treated, but only every 14 days when poor small ores of the first and second quality and poor coarse ores are treated. According to the results obtained in the year 1892,<sup>1</sup> furnace No. 1 at Idria (comprising 4 separate furnaces) treated in 24 hours 22.4 tons of poor and rich small ores, with a consumption of

<sup>1</sup> Mitter, *op. cit.*

130 cubic feet of wood, and a cost in wages of 17s. 9d. for every 10 tons of ore. The production of soot amounted to 3·3 per cent., and that of mercury to 204·2 tons. In furnaces Nos. 2 and 3, each furnace of 4 shafts treated in 24 hours 26·7 tons of poor small ore and pressed soot, with a consumption of 106·5 cubic feet of wood per 10 tons of ore. The cost of wages for this quantity of ore amounted



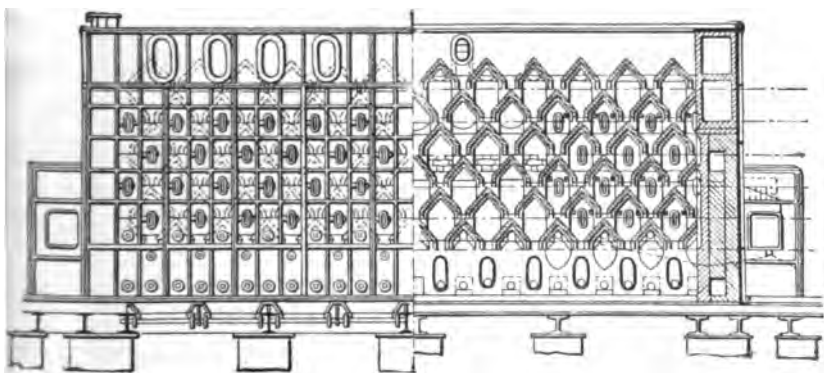
FIGS. 321 and 322.

to 14s. The production of soot amounted to 1·3 per cent., that of mercury to 117·7 tons. The loss of mercury in this furnace was 6·5 per cent. Furnaces erected later in Idria with only two winding paths for the vapours instead of four did not prove so successful as the older furnaces. Fine ores should as a rule be treated in Czernak furnaces, unless they have to be worked in long-bedded calciners on account of the production of too large quantities of flue-dust.

*The Czermak-Spirek Furnace*

The Czermak furnace has been improved by V. Spirek so far as drying the ores, distributing the air and furnace gases, and regulating the gas current are concerned; the improved furnaces have been introduced with success in Italy, and are being at present erected in Almaden.

The construction of the large Czermak-Spirek furnaces at present in use at Siele and Cornacchino, Monte Amiata, is shown in Figs. 323 to 327.<sup>1</sup> This is a double furnace divided into halves by a wall running along the longitudinal axis, and has the appearance of a rectangular iron chamber with two small chambers, one on either of the shorter sides. There is a system of oval openings which can



FIGS. 323 and 324.

be closed by movable lids at each of the longer sides. The side chambers contain the grates, and the firing may be either entirely with fuel such as coal, lignite, turf and wood, or partly with gas. The flue *b* in the middle wall of the furnace connects the two fire grates, and serves as the combustion chamber. All the walls of the furnace rest on plates of iron, *m*, *n*, turned up along the edge, so that they form a reservoir for the reception of the quicksilver which distils downwards. This can be tapped off into pots standing below.

The plates *m*, *n*, upon which the furnace is built, rest upon iron pillars which are provided with arrangements for the removal of the distillation residues. The columns supporting the iron pillars are

<sup>1</sup> *The Min. Ind.*, 1898, p. 568; *Il Forno Czermak-Spirek*, Torino, 1901; *Tipografia G. U. Cassone successore. Rivista La Chimica Industriale*; Anno II. No. 8, April, 1900.

capped with cast-iron plates to prevent the mercury from penetrating into the foundations. Each of the two long chambers in the furnace is divided lengthwise into three compartments by two walls of perforated stone pillars,  $p_1$  and  $p_2$ , and similar pillars abut inside the furnace on the middle wall and on the two long side walls. These pillars rest on iron plates 6 inches wide; they support the ore shelves or ridges  $s_1, s_2, s_3$ , and along with these form channels. There are six rows of ore shelves one above the other in each chamber, the lowest row comprising eleven whole and two half shelves, the second row twelve whole shelves, and so on for the other rows, the odd

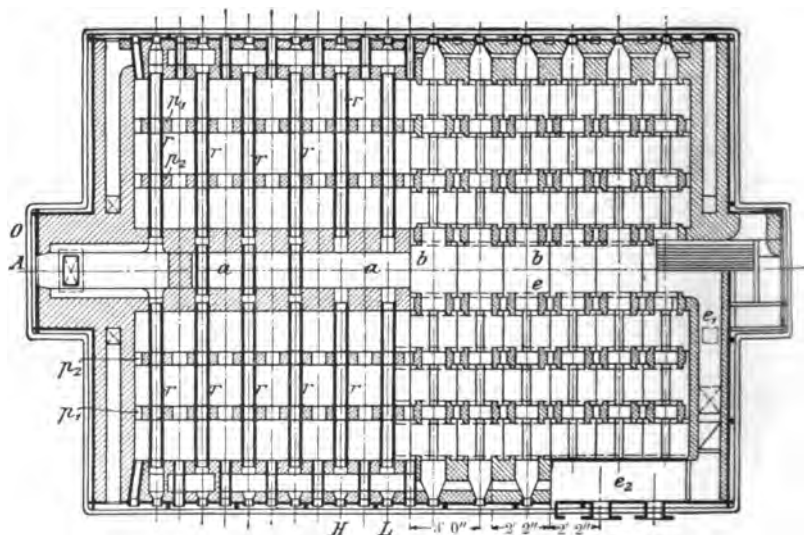


FIG. 325.

and the even ones being respectively alike. The surfaces of neighbouring ridges form a funnel with a short neck, as may be seen from Fig. 324, or better still from Fig. 320.

The ore rests 4 to 5 inches thick on the sloping shelves, and slips down periodically as the residues are removed from the bottom of the furnace, exactly in the manner described for the Czermak furnace. The residues are withdrawn by the discharging arrangement  $k$  (Fig. 327), the lower slots of which, by movement of the lever  $i$ , are brought in correspondence with slots in the slide  $h$ . The residues fall through the openings into the tipping boxes  $L$ , and thence into channels, where they are washed away by water. The furnace gases leave the combustion chamber  $b$  and pass through the lowest

row of channels, each of which is formed by three ridges  $s_1$ ,  $s_2$ , and  $s_3$ , placed one behind the other, by the corresponding pillars of the partitions, the side walls and the middle wall, and by the ore which blocks up the spaces between the tiles, in the manner shown in Fig. 320. The cross section of these channels, as seen in the same figure, is that of a diamond. The gases pass from this lowest row of channels, which they traverse lengthwise, into a vertical flue in the side wall. This opens into the next higher row of channels by two window-like openings, whereby the stream of gas is divided into two,

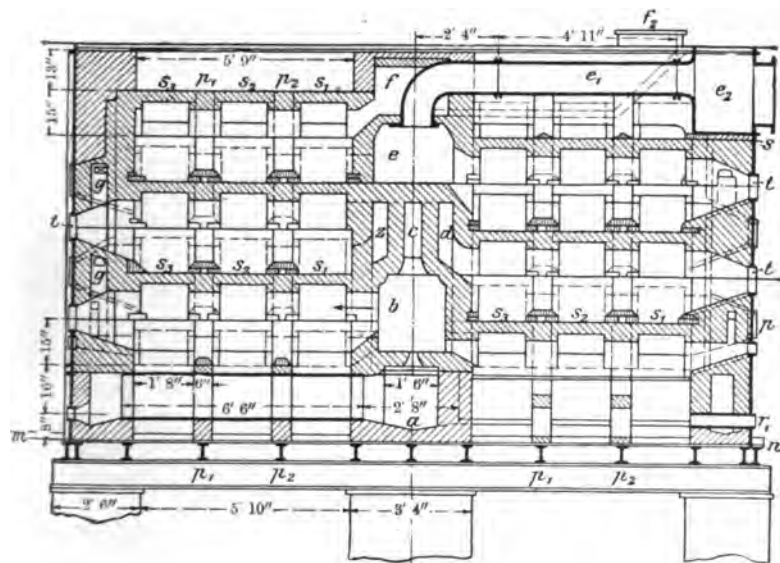


FIG. 326.

each entering one of the upper channels. In this way each higher lying channel contains half the vapours which pass through the lower one, so that constant mixing of the vapours, uniform heating of the charge, and a regular distillation are effected. After traversing the second row of channels, the gases rise through vertical flues  $d$  and  $z$  in the middle wall, are divided in similar fashion in the third row, escape from this through the fourth row, and eventually reach the main flue  $e$ . Thence they pass through two cast-iron pipes  $e_1$  into the distributor  $e_2$ , and thence into the condensers through eight outlets.

The flue  $b$  has twelve openings on each side for the escape of the furnace gases into two chambers. The path taken by the gases in

the four rows of channels is  $4 \times 6$  ft. 3 ins. = 25 feet long. The ore-drying chamber is immediately above the channels, and like them is composed of ridge-like shelves. The water vapour given off in drying is led away by a separate flue. If the ore does not slip through the furnace fast enough, then distillation vapours escape from the fourth row of channels into the drying chamber, and are led to the condensers through the flues  $f$  and  $f_2$  and through two special pipes. The ore is completely freed from water in the drying-room, and so much heat is absorbed in this process that the temperature of the gases which

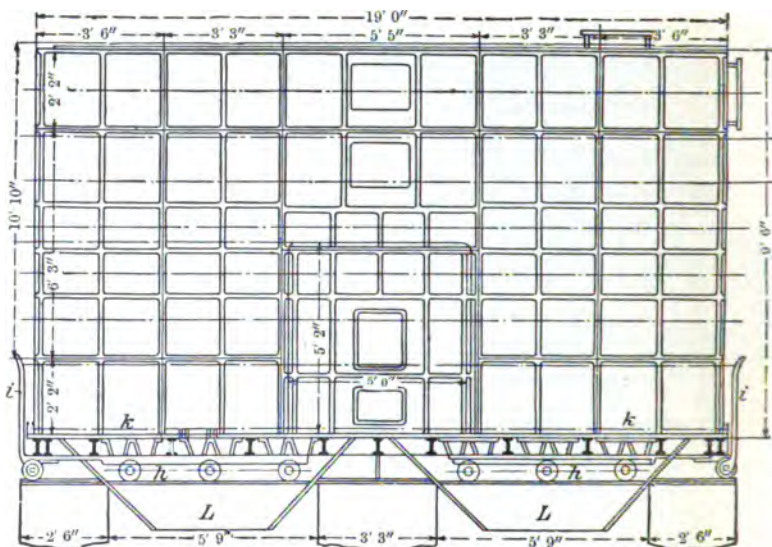


FIG. 327.

heat this chamber is brought down to  $360^{\circ}$  C. By means of this device it is possible to treat clayey ores in this furnace.

The space for the reception of the distillation residues is under the bottommost row of channels and is roofed by the ridges of these. It is connected with these channels, and also with the flue  $b$ , by vertical flues in the side walls, this arrangement ensuring on the one hand the drawing-off of any mercury vapours, and on the other the decomposition of any unaltered cinnabar in the residues. The space for the residues in each chamber is provided with twelve cast-iron pipes of elliptical section, which serve for warming the air for combustion and for cooling the residues to a temperature of less than  $100^{\circ}$  C. The air heated in these pipes to over  $300^{\circ}$  C. passes through the air chamber  $a$  to the fire grates and thence into the combustion chamber



and the flue *e*. The furnace gases are mixed with previously heated air in the combustion chamber *b*, so that complete combustion is made possible. As the two grates are fired alternately, the production of soot is greatly lessened. Uniform distribution of the furnace gases in the twenty-four channels of the furnace is brought about by means of the fire-brick slides *g*, which work in the upright flues of the side walls of the furnace. Sight holes *t* in the side walls enable the process inside the furnace to be observed, and allow of the introduction of iron bars to remove obstructions. In the two lower rows, where the temperature attains to 600–800° C. and the ore tends to sinter, frequent observations must be made and any blockage cleared away, but in the two upper rows of channels, where the temperature is only from 400–600° C., the ore slips down without hindrance. The temperature in the combustion chamber is 800–900° C., in the lowest row of channels 700–800° C., in the second row 500–600° C., in the third row 500° C., in the fourth row 360–400° C., and in the main flues and educts 200–360° C. The drying-room, heated from below by furnace gases, has a temperature of 100–200° C.; it is charged with ore through openings in the roof, and ore is piled 1 foot thick above these openings so that no vapours can escape. If crusts of ore form in the upper part of the charge they are broken up with thin iron bars, and the ore then sinks into the chamber proper.

The percentage composition of the gases leaving the furnace, apart from their mercury content, is given by Spirek as follows:—

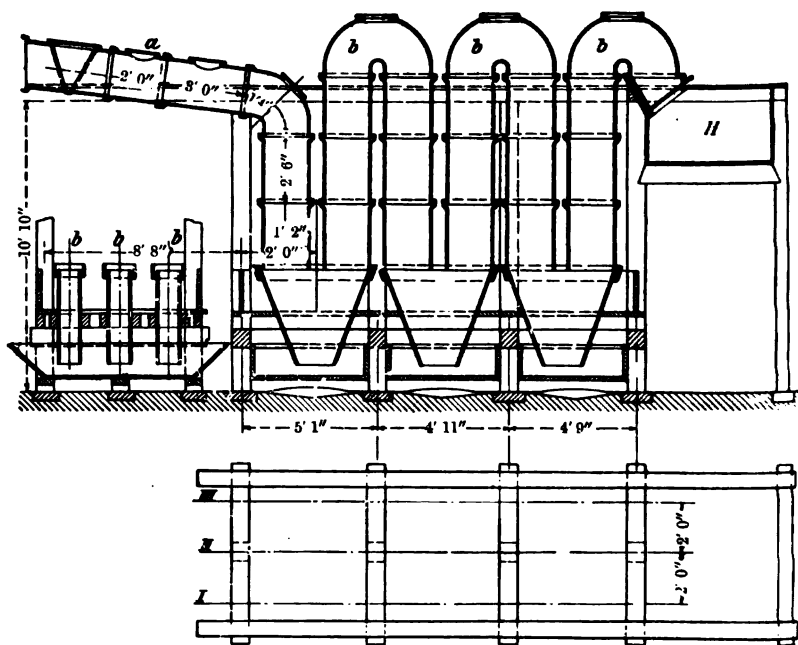
	I.	II.	III.
CO <sub>2</sub> . . . . .	16	20	22
CO . . . . .	2	1.5	0.5
Air . . . . .	26	25	21
N . . . . .	54	53	51

The pressure of the vapours within the furnace is kept below that of the atmosphere by means of a fan, the difference of pressure for the escaping gases being about 4 inches of water. The ores treated at Siele and Cornacchino in these furnaces are up to 1½ inches in size; those above this in size are treated in shaft furnaces as lump ore. If the moisture exceeds 7 per cent., ore destined for the Zermak furnaces must be specially dried, either by the sun in summer or on separate drying hearths in winter, before being charged into the drying chambers.

The capacity of the furnace depends on the nature of the ore and its mercury content. The poor clayey ores at Siele are withdrawn from the furnace every 3 hours, the sandy and calcareous ores at

Cornacchino every 2 hours, so that the capacity per 24 hours is 12-16 tons at Siele and 20-26 tons at Cornacchino. The furnace always contains 45 tons, so that the ore remains in it 89 and 41 hours respectively. Two men are needed to work the furnace, one for firing, the other for charging, in a 12-hour shift.

Besides the large Czermak-Spirek furnaces, there are others of intermediate size and small ones in use in Italy. The former at Montebuono, with six rows of ridges, put through 8-12 tons of ore in 24 hours; the latter serve for the treatment of richer ores and those



FIGS. 328-330.

residues containing 15-30 per cent. of mercury which are got by compression of the soot. The dimensions of the small furnaces are only  $\frac{1}{12}$ th those of the large ones, and are conditioned by the smaller quantity of rich ores at disposal. It is found more profitable to treat the rich ores by themselves than along with the poor ores; less fuel is consumed thereby, and the yield of quicksilver is good, amounting even in the first condenser to 90 per cent. The ores treated in these various furnaces contain from 0.4 to 86 per cent. of mercury.

The condensers in use are those introduced by Czermak in 1878; their construction is shown in Figs. 328 to 330. They consist of cast-

iron pipes of elliptical section, protected against acid liquors by a lining of concrete. By means of these pipes the vapours are speedily cooled to  $100^{\circ}$  C. The flue coming from the furnace is shown at *a*: *b, b* are U-shaped pipes from which the vapours escape into the wooden flue *H*. In the case of the large furnaces the condenser is divided into two portions connected by a wooden flue, and these are cleaned out alternately, one part weekly, the other monthly. This can be done without difficulty by cutting out one-half of the condenser by means of slides at the beginning and end of each row of pipes. The lid is removed from the part which has been put out of action, and the now open pipes are cleaned out with scrapers, besoms, and finally with a jet of water. The gases escape from the second condenser into wooden flues not more than 6 feet high, and placed for convenience sake about 6 feet above the ground. These replace the condensation chambers, and collect a poor soot from which yearly about 4,400 lbs. of quicksilver are extracted. The quicksilver losses in this method of working amount to 6 per cent. when the condensers are new, but only from 4 to 5 per cent. when the condensers have become permeated with the mercury. The costs of furnace and condenser for the three sizes of furnace mentioned above are 38,000, 32,000, and 5,000 francs respectively. At Siele, where ores averaging 1.2 per cent. of mercury are treated, the amount of ore worked off daily per furnace is 16, 8, and 2 tons for furnaces of large, medium, and small size respectively. Besides the Czermak-Spirek furnaces mentioned above, there are in use at present a large and a small one at Cornacchino, a medium-sized one at Montebuono, and two large and two small ones at Abbadia, S. Salvatore.

### *The Extraction of Mercury in Reverberatory Furnaces*

Reverberatory furnaces are inferior to the above described shaft furnaces in every respect. They are employed for small ore which yields too much flue dust when treated in shaft furnaces; also for coarser ore which decrepitates readily in the shaft furnace, and for ores that readily sinter. The first reverberatory furnaces were constructed in 1842 by Alberti in Idria. The last of these Alberti furnaces was discontinued in the year 1887. In 1871, the first iron-clad reverberatory furnaces heated from beneath the hearth were built at Idria by Exeli, which were followed in the year 1879 by Czermak's long-bedded calciners. The latter were remodelled in 1888 by Spirek, and thus received their present form. If the nature of the ore necessitates the employment of reverberatory furnaces,

long-bedded calciners should as a rule be employed. The Alberti furnace, the Exeli reverberatory furnace, and the reverberatory furnace at present employed in Idria will be considered in some detail. Reverberatory furnaces are not in use either in Spain or in America.

### *The Alberti Furnace*

The construction of these furnaces is shown in Figs. 331 to 333, which represent two furnaces lying side by side. *a* is the firegrate.

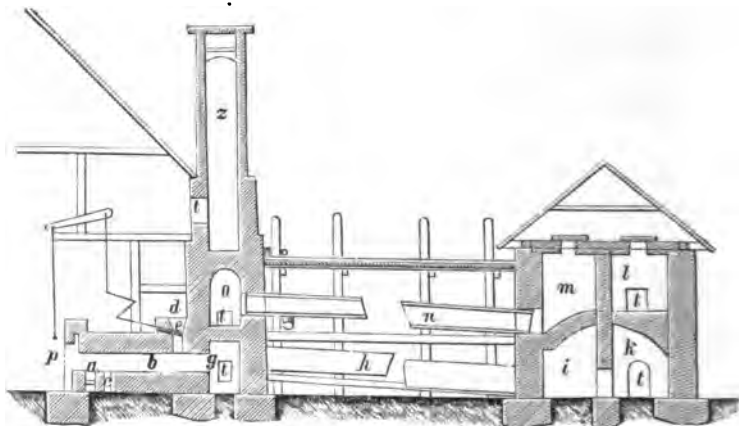


FIG. 331.

*f* the hearth 13 feet 6 inches long and 7 feet 3 inches broad; *p* is the working door, *c* a chamber into which the distillation residues can be emptied, *d* the charging hopper provided with a slide. The gases and vapours first pass into the brick chambers *g*, then through the iron pipe *h*, 27½ inches in diameter, into the brick chambers *i*, after which they traverse the chambers *k*, *l*, *m*, pass from the latter by means of the iron pipes *n*, into the chambers *o*, and lastly into the stack. In the latter there are compartments *p*, *q*, *r*, which the gases are compelled to traverse before being allowed to escape, which they do through the openings *s*. Water is allowed to trickle upon the iron pipes; *t* are manholes. The quicksilver collects in reservoirs built in the brickwork of the chambers. The soot is deposited in the iron pipes and in the chambers, and is

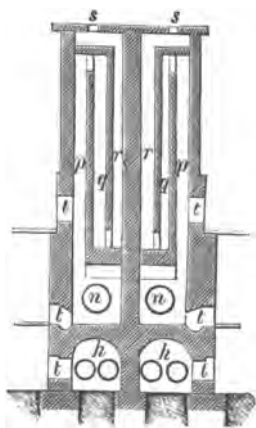


FIG. 332.

removed from them from time to time. In this furnace, ore fines with 1 per cent. of mercury and also soot were treated. The furnace received charges of 1.1 tons, three of which were always in the furnace at the same time. These charges were drawn and pushed

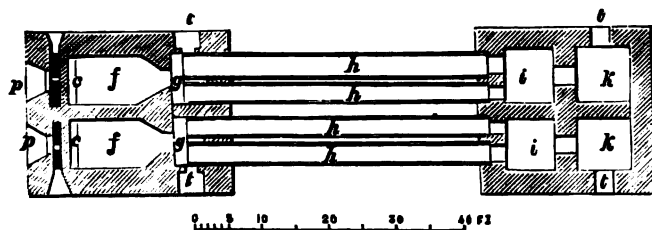


FIG. 333.

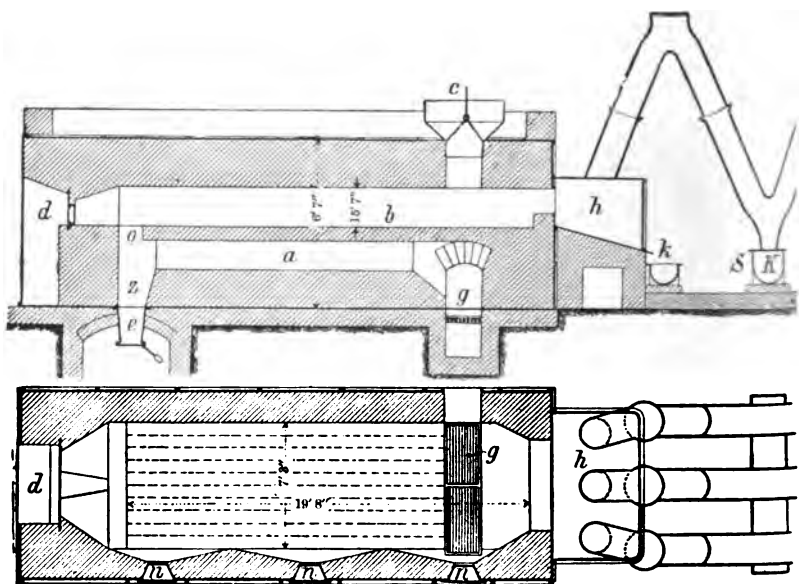
forward every 4 hours. In 24 hours, 6.6 tons of ore were treated with a fuel consumption of 106 cubic feet of wood, or of from 0.6 to 0.7 ton of lignite. The loss of mercury amounted to 14.80 per cent. when treating coarse small ore containing 0.4 to 0.6 per cent. of mercury. There were 12 of these furnaces in Idria, which have been, as mentioned above, replaced by the iron-clad calciners.

### *Iron-clad Reverberatory Furnaces.*

The first of these iron-clad, long-bedded calciners were built in 1871 by Exeli, and were used up to 1877 for treating the rich soot residues and ores. The construction of this furnace is shown in Figs. 334 and 335, in which *g* is the grate; the flame traverses first the flues *a* beneath the bed of the hearth, and then passes through the aperture *o* and over the hearth *b*, 20 feet long and 7 feet 3 inches broad. After having passed over the latter, the products of combustion, together with the other gases and vapours, enter the cast-iron box *h*, cooled by a stream of water, the floor of which is steeply inclined and covered with cement. The quicksilver, which condenses in it in considerable quantity, collects in the pan *k*. The gases and incondensed vapours pass into 3 rows, lying side by side, of cast-iron Y-shaped pipes, 18½ inches in diameter, which are provided with cast-iron boxes *s* for the collection of soot and mercury. From the pipes the gases enter 2 brick condensing chambers, and from the latter they pass into a system of flues common to all the chambers, and thence into the stack; *d* and *n* are working doors; *c* is the harging hopper. The distillation residues are dropped through the

opening *o* into the pocket *z*, and drawn off at *e*. This furnace, which treated rich materials, namely, ores containing 3 to 10 per cent. of mercury and soot residues, put through in 24 hours from  $2\frac{1}{2}$  to 5 tons of ore according to their contents of mercury, with a consumption of 106 cubic feet of wood. The loss of mercury amounted to 10 to 12 per cent.

This furnace was superseded in 1888 by the Czermak furnace as altered by Spirek, which is the furnace now employed. Its construction is shown in Figs. 336 to 339, Fig. 336 showing a longi-



FIGS. 334 and 335.

tudinal section, 338 a plan, 337 a cross section on the line *A-B*, and 339 a cross section on the line *C-D*. Two furnaces are united in one block. The furnace stands on a dish of riveted sheet-iron; *a* is the firegrate; the flame passes in flues *b* under the bottom of the furnace, and then passes over the hearth *c*, which is 18 feet long and 7 feet 6 inches wide, and is built of tiles 1·2 to 1·6 inches thick. The gases and vapours pass through 3 openings into the condensing appliances, which consist of a series of tubes made of glazed stoneware followed by wooden chambers; *t* is the charging hopper. The distillation residues are drawn off at *z*. The condensers, consisting of Y-shaped tubes, are similar to those in the Idrian furnaces and the shat-

furnaces, except that there are only 4 rows of tubes with 6 tubes in each. The construction of the condensers and the method of connecting them with the furnaces and the dust chambers is shown in Figs. 340 and 341. The method of connecting this furnace, each pair of which forms one block, with the condensers and the dust chambers is shown in Fig. 341, in which *O, O* are the furnaces, and *a, a* are the outlet pipes through which the gases and vapours from the furnace enter the distributing pipe *b*; *c, c* are the vertical condensing pipes, and *d, d* the dust chambers. The latter are made of boards 2 inches thick, and are supported on brick pillars *p*, the floor of the chambers being protected by a layer of Portland cement 2 1/4 to 3 1/2 inches thick. The floor beneath the condensers is concreted, there being gutters in

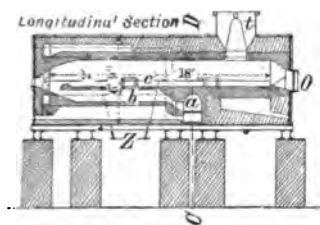


FIG. 336.

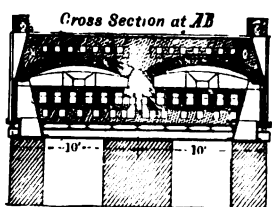


FIG. 337.

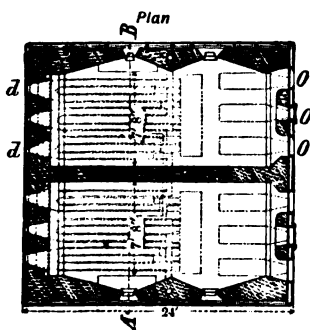


FIG. 338.

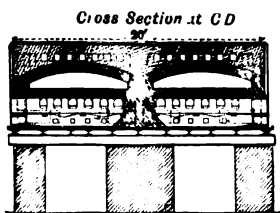
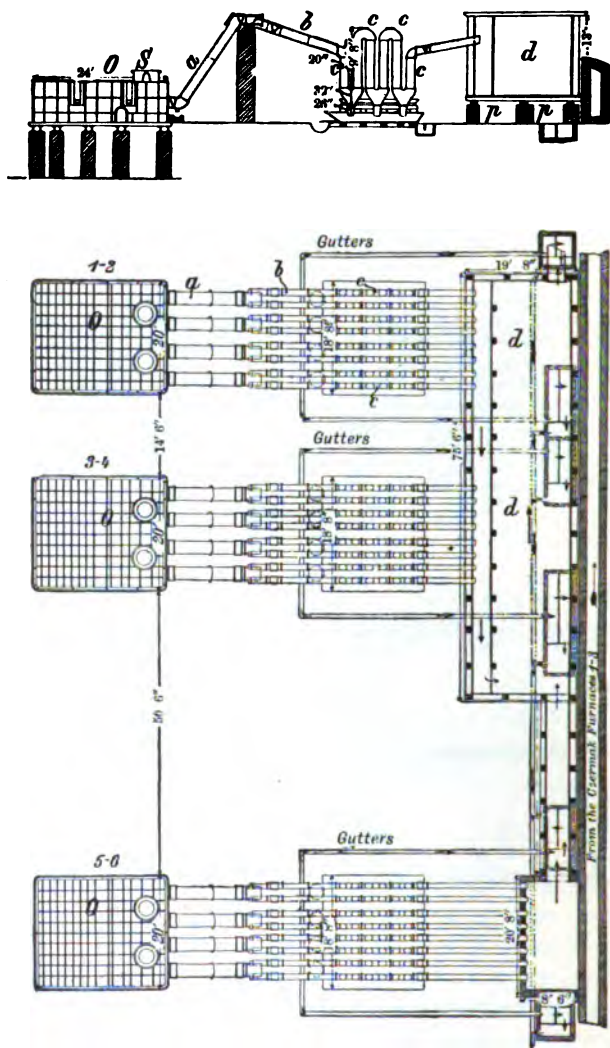


FIG. 339.

the concrete by means of which the condensed water and the wash-water is run into sumps. The latter are also built of concrete and are cemented twice a year. The condensers are cleaned out every fortnight. These calcination furnaces serve for the treatment of fine ores making very much dust and of ores that decrepitate in shaft furnaces, it being impossible to treat these classes of ore in any form of shaft furnace. The residues are drawn out and new ore is charged every

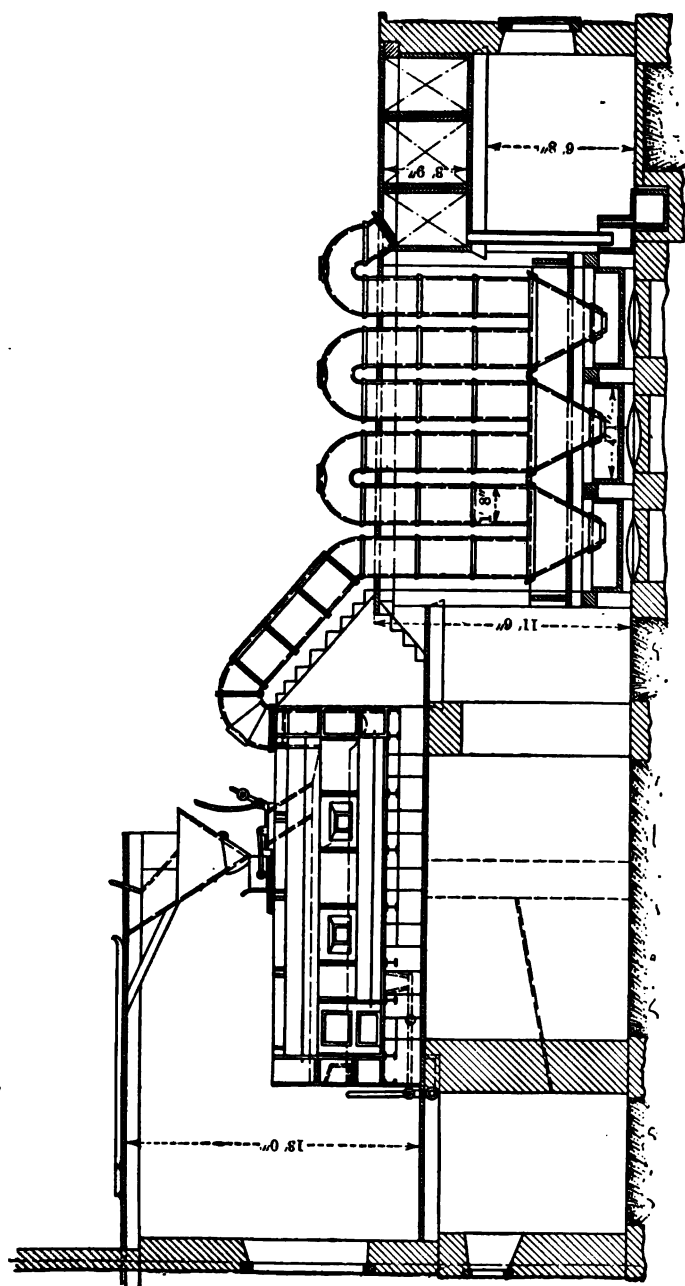
2½ hours. These furnaces treat in 24 hours 6·6 tons of poor ore and soot. The consumption of fuel amounts to 148 cubic feet of wood per 10 tons of ore. A pair of furnaces is served by 3 men in an 8-hour shift,



FIGS. 340 and 341.

viz., one fireman, one labourer for wheeling in ores, and one for removing the residues; wages vary from 20s. to 22s. per 10 tons of ore. The production of soot amounts to 1·9 per cent. The loss of mercury





Figs. 342 and 343.

is 8 to 9 per cent. It is evident from these figures that these reverberatory furnaces are more expensive to work than the Idrian furnaces. On account, however, of the reasons above given, their employment cannot be dispensed with.

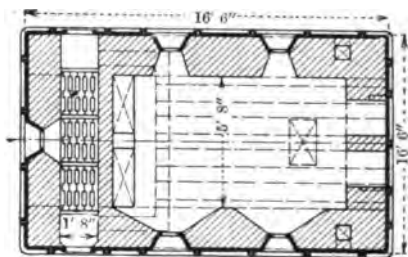


FIG. 344.

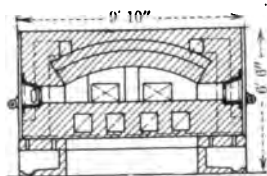


FIG. 345.

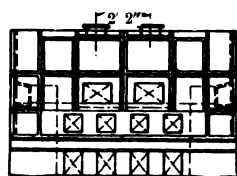


FIG. 346.

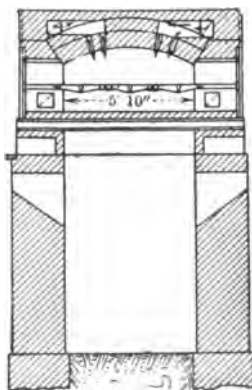


FIG. 347.

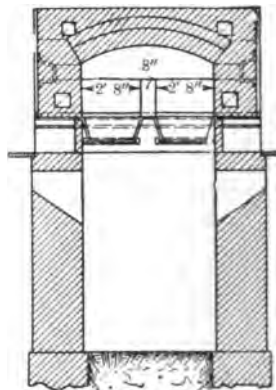


FIG. 348.

The arrangement of a recent calciner with condensers as designed by Spirek and used at Taghit, in Algeria, for the treatment of mercury-bearing lead ores, is shown in Figs. 342-349.<sup>1</sup> These figures are self-explanatory. Nos. 342 and 343 give a longitudinal view of

<sup>1</sup> Communicated by the director at Siele, Herr Spirek.

the furnace with Czermak condensers and wooden flues, 344 is a plan of the furnace and grate, 345-347 are sections at different places, 348 is the back view of the furnace, and 349 the section through the condenser.

*Extraction of Mercury in Shaft Furnaces Proper.*

Shaft furnaces proper, or those furnaces in which ore and fuel come into direct contact, work continuously, and when carbonised fuel is employed have the advantage, as compared with externally fired furnaces, that the production of mercurial soot (on account of there being no carbonaceous soot present in the products of combustion) is a very small one, in consequence of which the direct production of mercury is comparatively high. They should, therefore, be used as a rule for the treatment of lump ores in those cases in which carbonised fuel, especially charcoal, can be cheaply obtained. They are suitable both for lump ores and for briquettes made of small ore; they are used with satisfactory results at Monte Amiata in Tuscany and at Idria, where the externally fired furnaces of Exeli and Langer have been converted into true shaft furnaces by bricking up their fireplaces. In addition to these, shaft furnaces are used at Ripa, Castellazara, and Valalta in Italy, as also at St. Annathal, near Neumarktl in Carniola. At Almaden they have only been used experimentally (Pellet furnace). The oldest shaft furnace is the so-called Hühner furnace, which was introduced in the year 1849 in Idria, where it was in operation up to 1852. The construction of the Idrian Hühner furnace is shown in Figs. 350 to 352, in which *k* is the shaft 36 feet high and 4 feet in diameter; *m* is an inclined movable grate upon which the column of ore rests. In order to remove the distillation residues, a certain number of the firebars can be withdrawn, so that the former can drop into waggons placed below the grate; *n* is the charging hopper; *o* are brick condensing chambers with concave floors inclined to one side in order to enable the mercury to run off. The chambers are provided with a roof of cast iron cooled with water; they are 18 feet 6 inches high, 6 feet broad, and 4 feet 3 inches long; *p* and *q* are sections of the stack, which is 6 feet 3 inches by 4 feet in plan. Alternate layers of ore and charcoal are charged into this furnace. At intervals of  $1\frac{1}{2}$  hours the distillation residues are removed and a corresponding quantity of fresh ore charged. This furnace was replaced by the Valalta furnace, to be described presently.

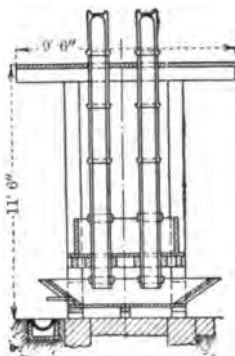
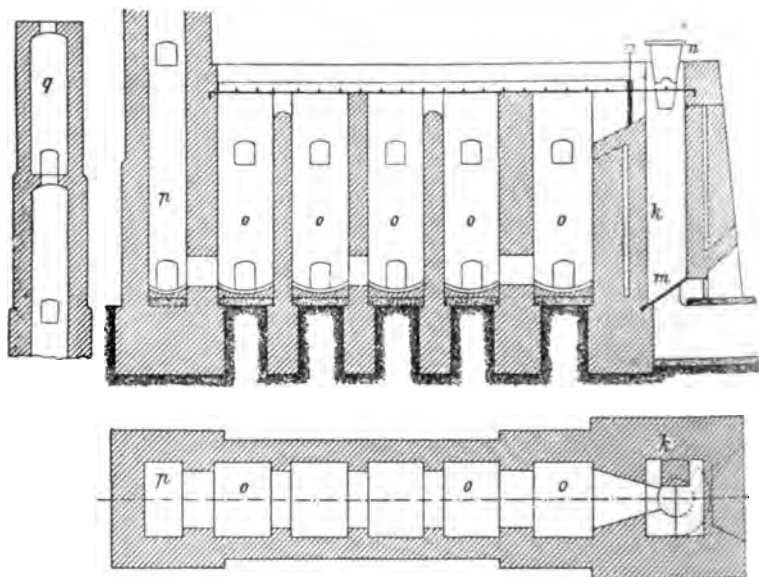


FIG. 349.

The furnace at Castellazara, near Santaflori in Tuscany, is shown in Fig. 352. The shaft has a height of 7 feet 3 inches above the grate, its diameter being  $15\frac{1}{4}$  inches. The distillation residues are



FIGS. 350 and .351.

withdrawn through a lateral opening above the grate. The gases and vapours traverse three condensing chambers one after the other, the floors of which are formed of cast-iron pans. The mercury that

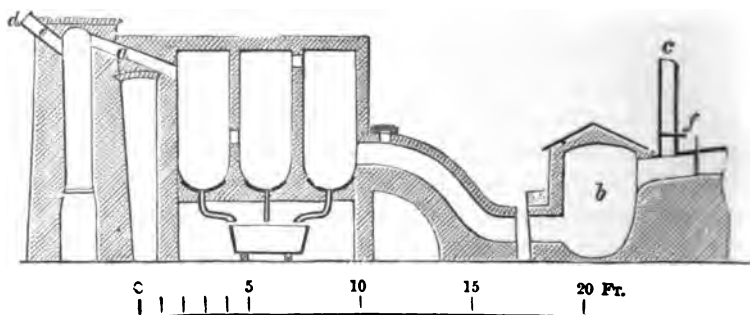


FIG. 352.

settles in the latter is drawn off by means of pipes provided with cocks into waggons placed beneath them. From the last condensing chambers, the gases and vapours enter another chamber *b*, and

thence pass to the stack *c*. Ores were treated in this furnace which contained from 0·3 to 0·4 per cent. of mercury.

The furnace of Valalta in Venice,<sup>1</sup> which was used also at Idria from 1868 to 1878, is provided with wooden condensing flues cooled

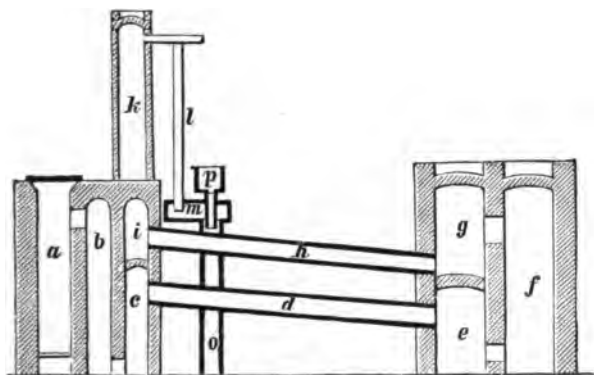


FIG. 353.

by water. Its construction is shown in Fig. 353; *a* is the shaft, 21 feet 4 inches high and 4 feet broad. The gases and vapours pass through the chambers *b* and *c* into the wooden pipe *d*, 3 feet 3 inches

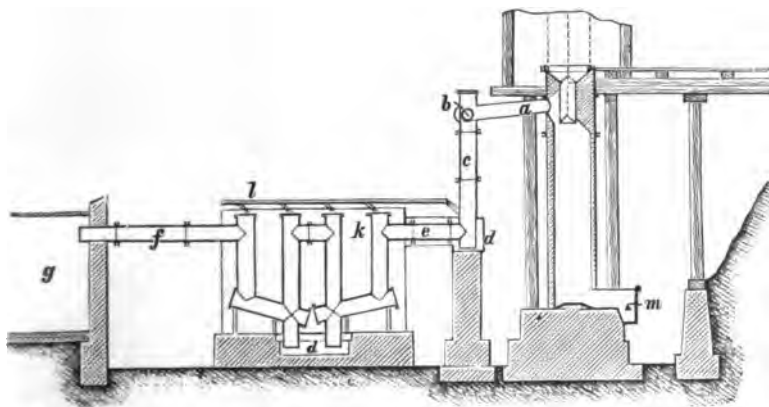


FIG. 354.

broad and 50 feet 6 inches long, thence into the chambers *e*, *f* and *g*, from the latter of which it passes into the upper wooden pipe *h*, also cooled by water, which possesses the same dimensions as the lower pipe. From this it enters the chamber *i*, and thence

<sup>1</sup> *Oesterr. Zeitsch.*, 1862, p. 195; *Berg- und Hüttenm. Ztg.*, 1864, p. 284; 1868, p. 32; *Eng. and Min. Journ.*, 1872, vol. xiv., Nos. 11 and 12.

the stack *k*. The pipes are short, conical in shape, and set one into the other. The draught is produced by means of a water trompe *p*, connected with the stack, in the water tube *o* of which the last portions of mercury are collected. These furnaces treat in 24 hours 9 tons of ore containing 0.45 per cent. of mercury, with a consumption of fuel equal to 20 per cent. The loss of mercury is said to amount to 22.3 per cent.

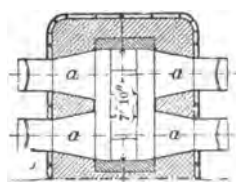
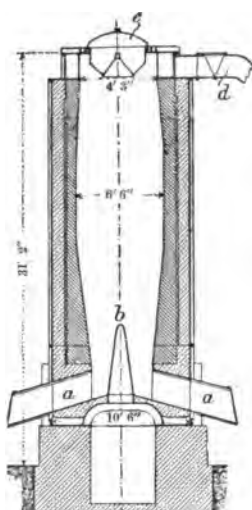
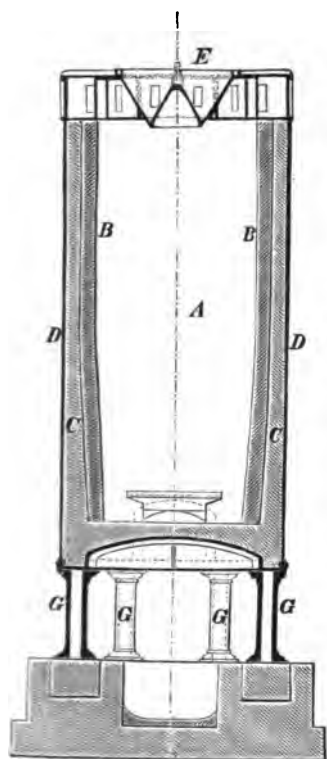
The furnace at St. Annathal, Carniola,<sup>1</sup> is shown in Fig. 354. It is square in horizontal cross section, 4 feet by 4 feet, its height amounting to 30 feet 6 inches. The gases and vapours traverse two rows of cast-iron pipes contained in a cooling chamber *k*, and thence pass through wooden pipes *f* into a chamber *g*. The latter is connected to a water trompe which produces the requisite draught. The greater part of the mercury is collected in the box *d*, and the distillation residues are removed through man-holes *m*, of which there are three. The ore contains 0.8 per cent. of mercury; it remains for 46 hours in the furnace, which takes 23 charges of 11.2 cubic feet of ore and 1.76 cubic feet of charcoal. The distillation residues are removed from the furnace every two hours, when a corresponding quantity of fresh ore is charged.

The furnace built at Idria in 1888, which was replaced in 1892 by the new Novak shaft furnace on account of its unsatisfactory results, is shown in Figs. 355 to 357. *A* is the shaft, *B* being the shaft lining, *C* the retaining wall, *D* the iron casing; *G* are cast-iron columns which support the shaft; *E* is the charging apparatus; *F, F* are openings through which the distillation residues are drawn out of the furnace. The gases and vapours pass through the tube *H* into the Czermak condenser, which consists of Y-shaped tubes *J*, made of clay. The condensed mercury collects in the vessel *L*, which is filled with water. From the condensing tubes the gases and vapours pass into the brick chambers *K*.

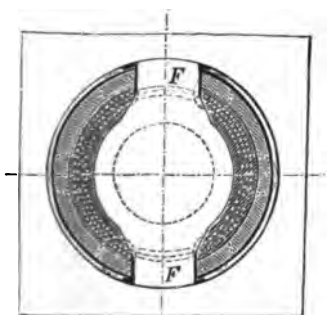
This furnace was replaced in 1892 by the very successful new Novak furnace. This is rectangular in cross section and has four openings for the removal of the residues. The retaining wall is 24 inches thick, the inner wall 8 inches. The construction and dimensions are shown in Figs. 358 and 359. Three of these furnaces are united to form a block; *a* are the openings for drawing off the residues, *b* is a roof-shaped ridge on the bottom pierced with numerous small openings. Through the latter, air enters from the bottom of the furnace and, thus heated, passes into the furnace through the above-named holes; *c* is the charging hopper, *d* the escape pipe for

<sup>1</sup> *Kärnthener Zeitsch.*, 1877, p. 332.

the gases and vapours, which thence enter the stoneware condensers and pass onwards into dust chambers. In this furnace poor ore down



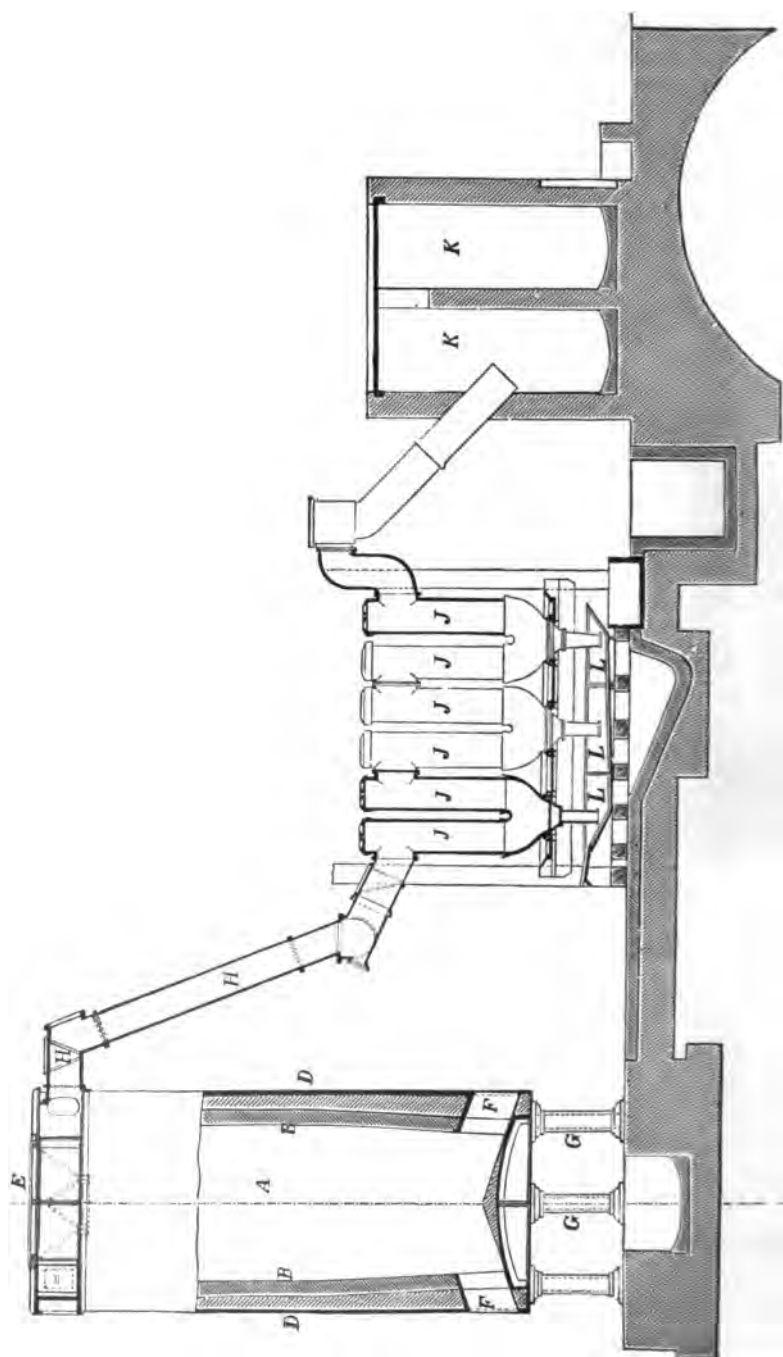
FIGS. 358 and 359.



FIGS. 355 and 356.

to 0.67 inch mesh is treated, together with pressed soot; the furnace, which is charged every two hours, will put through 12.1 tons of ore in 24 hours. For 10 tons of ore 1.6 tons of charcoal are consumed. 4.2 men are employed for two shaft furnaces on an 8-hour shift. The cost of wages per 10 tons of ore amounts to 13s. 4d. The production of soot amounts to 0.5 per cent., the loss of mercury to 7 to 8 per

cent. The condensers, as in the other Idrian furnaces, consist of Y-shaped tubes of stoneware cooled by water. They are oblong in





cross section, 0.8 inch thick, and are supported in wooden frames. The various pipes are joined together by means of cement. The lower contracted branches dip for about two inches into water contained in cast-iron boxes, which are lined with cement. For each furnace there are 4 rows of tubes, with 6 tubes in each. The gases and vapours enter at a temperature of  $200^{\circ}$  to  $300^{\circ}$  C., and finally escape at a temperature of  $8^{\circ}$  to  $12^{\circ}$  C. From 4.4 to 6.6 gallons of water are used per hour per furnace for cooling purposes. When poor coarse ore is being treated, the condensed mercury is swept out every 14 days from the condensers into the boxes lying beneath them, but every 4 or 5 days when pressed soot is being treated. The

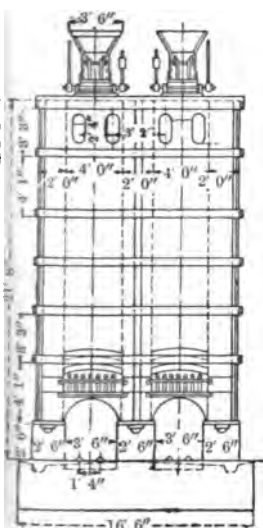


FIG. 360.

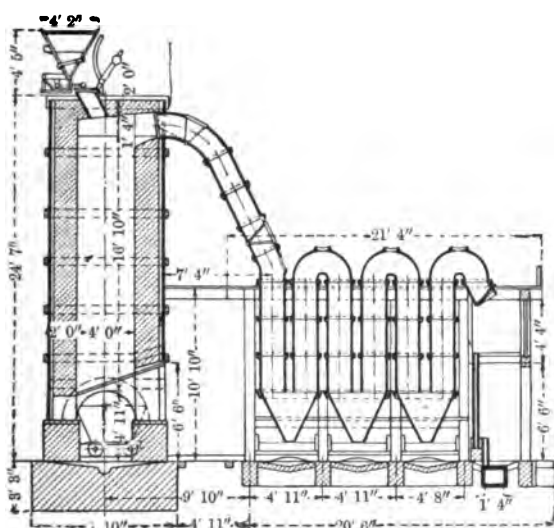


FIG. 361.

mercurial vapours escaping from the stoneware pipes are condensed in chambers constructed of wood and divided by partition walls into several divisions, the wooden walls being made air-tight by groove and tongue joints. The construction of the condensers, the method of connecting them with the shaft furnaces, and the dust chambers, are similar to those described on page 402. The stoneware condensers introduced by the chief works manager, Mitter, have completely replaced the iron condensers, which lasted only 1 to  $1\frac{1}{2}$  years, whilst the stoneware condensers last for any length of time, and cost only one-third as much as the iron condensers. They are made in Floridsdorf, near Vienna, at the factory of Lederer and Nesseny.



## THE EXTRACTION OF MERCURY IN RETORT FURNACES.

The extraction of mercury in retort furnaces is not to be recommended, on account of the injurious effects of the mercury vapours upon the workmen engaged. The losses of mercury are, moreover, no less than in modern shaft and reverberatory furnaces, their only advantage being that their first cost is less than that of the latter furnaces. On the other hand, the working costs are higher on account of their smaller capacity. The material of the vessels and of the condensers is cast-iron. These furnaces have been used for a while in Idria, Siele, Monte Amiata and California, but are probably nowhere in use at the present day. At Idria the furnace of Von Patera was used for a while experimentally. Its construction is shown in Figs. 365 and 366.<sup>1</sup> *A* is the muffle, 23½ inches broad, 29½ inches long and 9 inches high; *c* is the condenser made of sheet iron provided with an inclined floor along which the condensed mercury

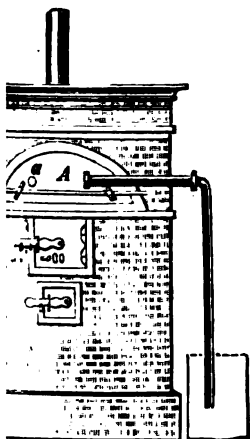


FIG. 365.

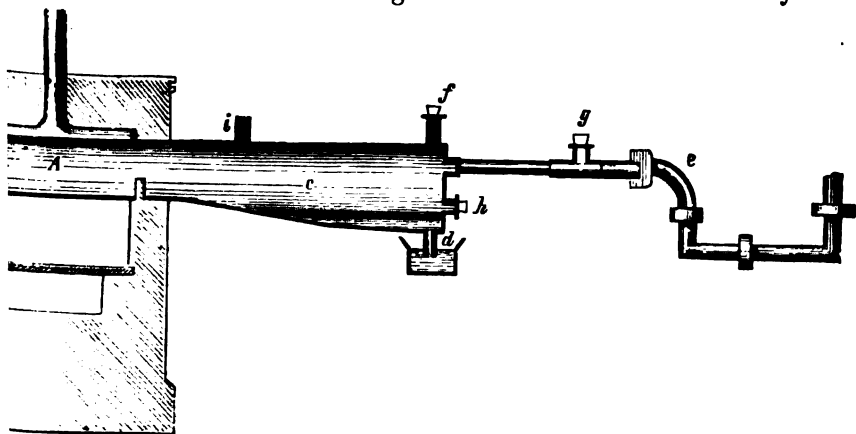


FIG. 366.

runs towards the pipe *d*, through which it enters the collecting pan placed beneath it. From this condenser the gases and vapours pass through an iron pipe into a system of clay pipes and thence into the stack; *f* and *h* are openings for cleaning out

<sup>1</sup> *Oesterr. Zeitschr.*, 1874, p. 291; *Berg- und Hütt. Ztg.*, 1874, pp. 91, 419.

the condenser, which can be closed by means of clay plugs; *g* is a short branch pipe in which a gold-leaf is suspended; in normal working, this may not show any coating of mercury; *i* is a short branch into which a thermometer can be inserted. The air required for oxidation is introduced through openings *a*. The charge of the muffle is said to have amounted to 1 cwt. of ore. The output, when ores containing 1.5 to 3.6 per cent. of mercury were treated, is said to have amounted to 90 per cent., whilst in the furnaces at present in use at Idria the output amounts to 91.75 per cent.

Spirek and Nathan introduced a furnace into Siele in 1896 which had the retorts arranged in two tiers. They were all connected to a central condensing chamber, and the pressure within was kept below that of the atmosphere. The distillation residues were discharged by special appliances and washed away by a stream of water. In these furnaces 1 ton of ore was worked off in 24 hours. These furnaces have been put out of action, since better results for ore and soot can be obtained by using the small Spirek furnaces.

At the Missouri Mine, near Pine Flat, and at the Lost Ledge Mine, in California, retort furnaces were used.<sup>1</sup> The furnaces at the Missouri Mine contained either two or three cast-iron retorts 9 feet 6 inches long, 12.5 inches high and 19 inches broad. These were charged with  $2\frac{1}{2}$  cwts. to  $3\frac{1}{2}$  cwts. of ore, containing from 1 to 2 per cent. of mercury. In 24 hours, 10 cwts. to 1 ton of ore were treated. The consumption of fuel per furnace was about  $3\frac{1}{2}$  cords of wood per 24 hours on the average. The gases and vapours were conveyed through an iron pipe into iron boxes open below, which dipped into an iron tank filled with water. In this tank, which was 3 feet long 24 inches broad and 24 inches high, the mercury was condensed. The furnaces and condensing appliances at the Lost Ledge Mine were similar except that the retorts, of which there were three in a furnace, were smaller, being only 5 feet long and holding only 183 lbs. of ore. They were charged every 4 hours. In 24 hours such a furnace treated about  $1\frac{1}{2}$  tons of ore.

#### THE EXTRACTION OF MERCURY BY HEATING CINNABAR WITH LIME OR IRON IN THE ABSENCE OF AIR.

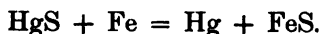
This method of mercury extraction has the advantage that the vapours of that metal are obtained in a concentrated condition, and are therefore readily condensed. The first cost of the furnace and condensers required is also lower than of those needed for the

<sup>1</sup> *Trans. Am. Inst. Mng. Engrs.*, 1875, vol. iii., p. 276.

extraction of mercury by heating cinnabar in the air. On the other hand, the residues contain more mercury, so that the output is thus reduced and the process gives no better results even with the most careful work than can be obtained with the other method. The costs of working are very high, in consequence of the necessity for employing reducing agents and for previously crushing the ore, as also on account of the high consumption of fuel and the small output of the retorts. The costs of repairs are also high, in consequence of the retorts becoming rapidly destroyed. The greatest disadvantage, however, may be considered to be the injurious effect of the fumes of mercury upon the workmen. Generally speaking the process is unsuitable for poor ores, and for rich ores it is in no way cheaper than the other methods of treatment, whilst for hygienic reasons it cannot be recommended even for rich ores. It should therefore only be employed when small quantities of very rich ores or soot have to be treated, and should be condemned for working rich ores upon a larger scale. The retorts in which the cinnabar is decomposed were first pear-shaped or bell-shaped, and were made of clay or cast-iron; later cast-iron alone was employed, and the retorts received the shape of those employed in the distillation of coal-gas. The condensers, which were formerly made of clay at some works, are now also made of cast-iron. The flux required for decomposing the cinnabar should as a rule be quicklime; iron or hammer scale have only been used exceptionally for decomposing the ore. Lime acts upon cinnabar at a red heat, as shown by the following equation:—



The action of iron is as follows:—



The process has been employed in California, in Idria, in the Rhenish Palatinate, at Monte Amiata and in Bohemia, and is still in use at present at Lattai in Carniola. It was given up in California on account of the above objections in the year 1850, and from that date up to 1860 was only used experimentally.<sup>1</sup> It was used in Idria for soot and rich ores up to 1882. At Moschellandsberg, in the Rhine Palatinate, and at Horzowitz, in Bohemia, it has been given up because the deposits found at those localities have been worked out.

At the American Mine, Pine Flat, California,<sup>2</sup> ores containing 2 per cent. of mercury were heated in cast-iron retorts of the shape

<sup>1</sup> Egleston, *op. cit.*, p. 112.

<sup>2</sup> Egleston, *op. cit.*, p. 811.

of gas retorts 9 feet in length, 2 feet in width, and 18 inches in height, in charges of 150 lb. with the addition of 10 per cent. of lime; 500 lb. of ore were put through in 12 hours. Even apart from the injurious effects upon the workpeople, the treatment of such poor ores in retorts must be condemned.

At Landsberg, in the Bavarian Palatinate, pear-shaped retorts were at first employed: they were 3 feet 3 inches in length, with

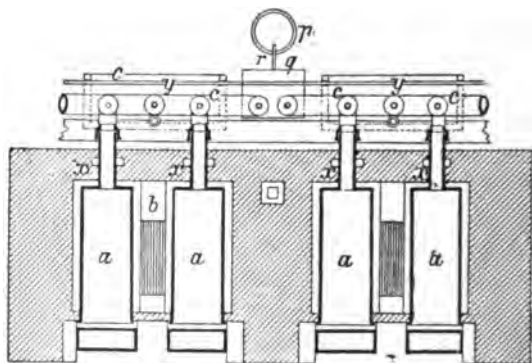


FIG. 367.

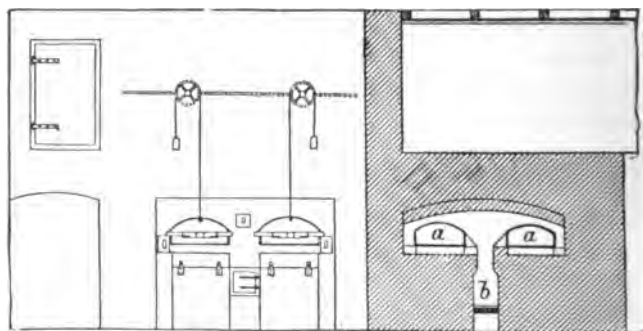


FIG. 368.

a maximum diameter of 18 inches, and 40 to 60 of them were placed in two rows in a galley furnace. The condensers were pear-shaped vessels of clay 16 inches long and  $9\frac{1}{2}$  inches maximum diameter, which contained a certain quantity of water. The charge consisted of 44 lb. of rich ore, 44 lb. of poor ore, and 18 to 20 lb. of burnt lime; such a charge was treated in from 6 to 8 hours. One part by weight of mercury was obtained from 80 to 120 parts of ore, according to the richness of the latter, with a consumption of 20 to 30 parts of coal. In 1847 Ure introduced

retorts of the shape of gas retorts. From these retorts the vapours were passed through iron tubes into boxes half filled with water, in which the mercury was condensed. The tubes dipped for 2 inches below the surface of the water. The charge of ore for a retort amounted to 5 cwts., and it was worked off in three hours.

At Horzowitz, in Bohemia,<sup>1</sup> the ore was mixed with hammer scale and treated in bell-shaped vessels. The charge was 55 lb. of ore and 27 lb. of hammer scale, which required 36 hours for their treatment.

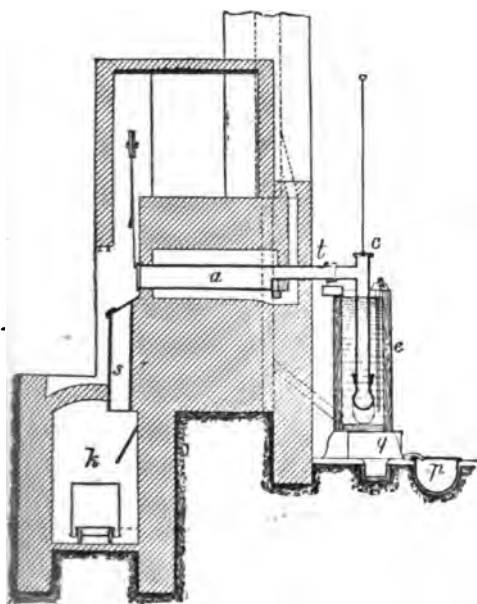


FIG. 369.

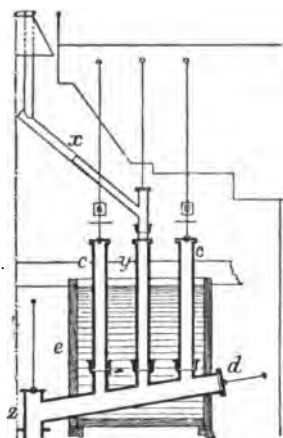


FIG. 370.

At Idria, in Carniola, a furnace was introduced by Exeli in 1869 and worked up to 1882 for the purpose of treating finely crushed ores and soot. This furnace,<sup>2</sup> the construction of which is shown in Figs. 367 to 370, contained two cast-iron retorts, *a*, 7 feet 4 inches long, 2 feet 3 inches broad, and 1 foot 1 inch high, which were closed at the back by means of a cast-iron cover coated with clay; *b* is the fire-grate. The vapours escaped through horizontal tubes *t*,  $6\frac{1}{4}$  inches in diameter, into vertical tubes, *c*, of the same diameter and 5 feet in height, which were provided with discs for cleaning them out, and which opened into an inclined collecting tube, *d*,  $9\frac{1}{2}$  inches in diameter. The vertical condensing pipes and the collecting tube are contained in a wooden

<sup>1</sup> Kerl, *Metallurgie*, vol. ii., p. 811.

<sup>2</sup> *Idrianer Festschrift*; Mitter, *loc. cit.*

cooling box filled with water. The condensed mercury flows through the inclined tube *d* into the tube *z*, and from the latter into a closed receiver *q*, filled with water, from which the mercury is syphoned off into the kettle *p*. The uncondensed gases pass through the middle tube *y* and the inclined tube *x* into the dust chamber and the flue; *s* is a vertical shoot through which the distillation residues can be dropped direct from the retorts into the vault *k* or into the waggons which

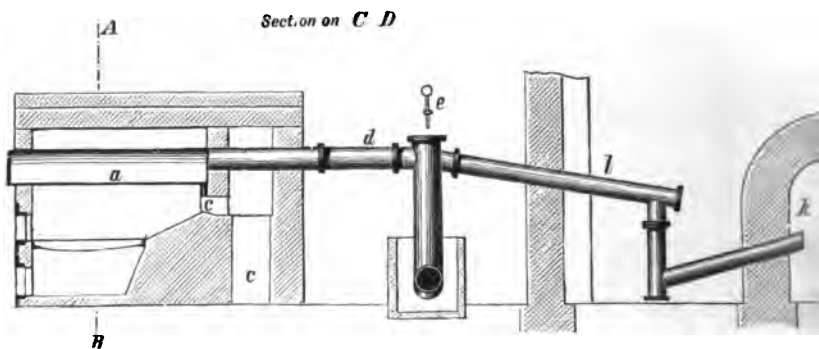


FIG. 371.

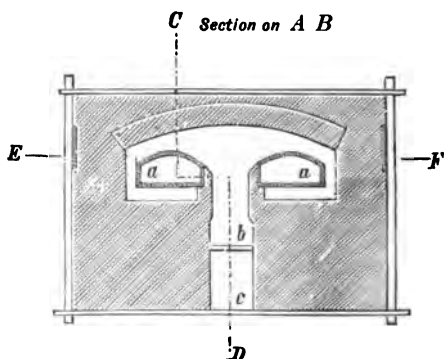
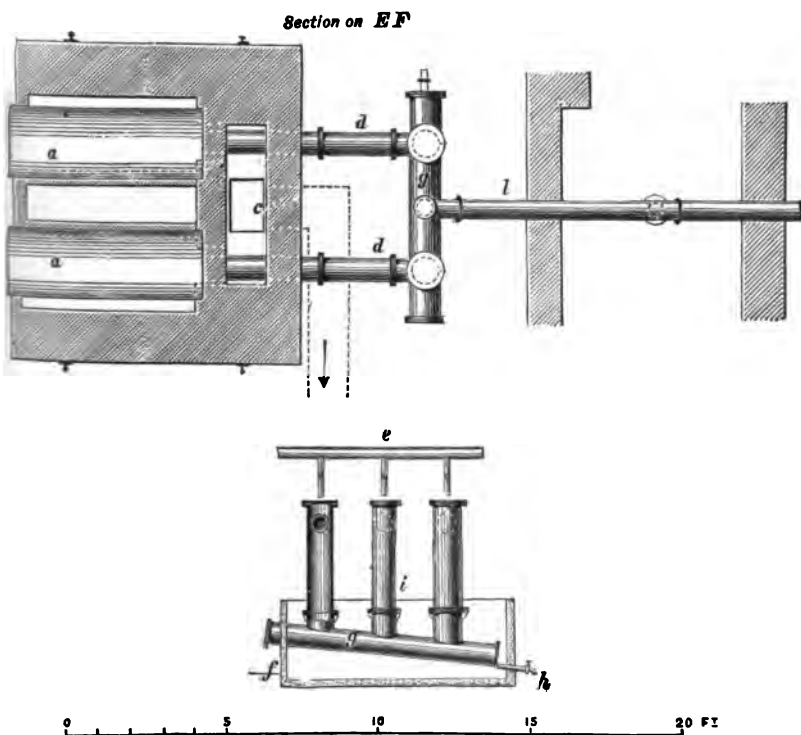


FIG. 372.

are run into it. In these furnaces fine ore with 10 per cent. of mercury and soot were treated. The material was mixed with lime in the proportion of 1.5 parts of caustic lime for every part of mercury contained in the ores, and then moulded into bricks in a special press. These bricks were dried and charged into the retort which held 108 bricks at a time, weighing altogether 300 lb. This charge was worked off in from 4 to 6 hours, according to the richness of the ores. The consumption of fuel per 24 hours amounted to 63.5 cubic feet of wood and 794 lb. of lignite.



At Littai, in Carniola, where the process is still in use, a furnace very similar to the Idrian retort furnace is employed. Its construction is shown in Figs. 371 to 374<sup>1</sup>; *a a* are the cast-iron retorts, *b* is the grate, *d* are the tubes through which the vapour passes into the condensing tubes or into the inclined tube *g*; *f* is the cooling tank, *i* is the tube for carrying off the uncondensed gases into the tube *l*, and thence into the dust chamber *k*. The ores contain on an average



FIGS. 373 and 374.

per cent. of mercury. They are crushed by rolls to 0·2 inch, and are charged into the retorts mixed with 5 or 6 per cent. of caustic lime, a retort taking a 2 cwt. charge, and the operation lasting 6 hours. In 4 hours 16 cwt. of ore are treated. One hundred and seventy parts by weight of fuel are used for 230 parts of ore, the fuel consisting of 0 per cent. duff and 20 per cent. pea coal. The loss of mercury is stated to amount to from 5 to 6 per cent.

At the smelting works at Siele and Connacchino at Monte

<sup>1</sup> Balling, *Metallhüttenkunde*, p. 502.



flame uniformly through the heating chamber, it is allowed to escape into the stack by means of three vertical flues, of which there is one above each retort. The mercury vapours escape through the cast-iron pipe *c*,  $4\frac{3}{4}$  inches in diameter, which is cooled with water, into a wooden box *e* filled with water, the liquid mercury running into the cast-iron receiver *f*, from which it flows continuously by the pipe *g*. The uncondensed vapours escape through the tube *d* into condensing chambers, in which there is a constant spray of water, and thence into the stack. The retorts hold 4 to 5 cwts. of ore and 88 lb. of lime, the proportion of lime being increased in the case of pyritic ores. The temperature is raised up to bright redness, and the treatment of the charge takes 7 to 8 hours. A ton of wood is used per ton of ore. When the ores contain up to 30 per cent. of mercury, the total cost of producing 2·2 lb. of mercury amounts to fifteen pence.

### THE PRODUCTS OF MERCURY EXTRACTION

The products of the process of mercury extraction are, in addition to mercury, mercurial soot, acid water, and distillation residues. The mercury is often rendered impure by mechanical admixtures, to remove which it is squeezed through canvas or leather. Mercury is sent to the market from the larger works in bottles of wrought iron with screwed stoppers. Their weight when empty amounts to 12 to 14 lb. The flasks contain 76 lb. of mercury in Europe and 76·6 lb. in California. In the smaller works mercury is also exported in bags made of two thicknesses of leather.

#### *Soot*

Soot ("*Stupp*"), as already mentioned, consists of the deposit upon the walls of the condensers, which is often formed in considerable quantities, and is a mixture of finely divided mercury, mercurial compounds, carbonaceous soot produced by the distillation of the fuels, and the bituminous and other impurities of the ores. The quantity of mercury in the soot may reach 80 per cent. The composition of various qualities of soot from different sources is shown in the following analyses:—

	IDRIA.		
	1	2 <sup>1</sup>	3
Hg . . . . .	3·12	14·59	0·92
HgS . . . . .	27·33	1·83	3·40
Hg <sub>2</sub> SO <sub>4</sub> . . . . .	7·32	3·06	6·10

<sup>1</sup> Teuber, *Oesterr. Zeitschr.*, 1877, p. 123; *Dingl.*, vol. ccxxv, p. 214.

According to Oser,<sup>1</sup> soot from the condensers of the Idrian externally fired furnaces contains :—

	Per cent.
Mercury removable by pressure . . . . .	40·95
Non-removable by pressure, and in the form of salts . . . . .	9·15
Sulphuric acid . . . . .	1·39
Mercuric sulphide . . . . .	4·32
Carbon . . . . .	3·31
Ashes . . . . .	9·33
Water . . . . .	31·55

The composition of soot from the condensers of the muffle furnaces of Patera, called by him *mercury black*, is shown in analysis No. 1, that of the flue soot from the flues leading to the stack and following the condensers is shown in analyses 2 by Patera and 3 by Teuber :—

	1	2	3
Mercury . . . . .	56·30	6·42	3·12
Mercuric sulphide . . . . .	0·70	2·20	31·10
Mercuric sulphate . . . . .	18·99	13·07	10·80
Mercurous chloride . . . . .	2·20	1·80	—
Sulphuric acid . . . . .	1·10	4·80	—
Magnesia . . . . .	—	1·10	—
Lime . . . . .	0·76	1·20	—
Ferric oxide and alumina . . . . .	trace	0·80	—
Calcium sulphate . . . . .	1·04	6·30	—
Basic ferric sulphate . . . . .	3·24	0·40	—
Soot and tar . . . . .	33·9	29·40	24·80
Water . . . . .	4·60	26·50	10·30
Ore residues . . . . .	11·41	3·80	—
Ferrous sulphate . . . . .	—	—	6·02
Magnesium sulphate . . . . .	—	—	7·50
Sodium sulphate . . . . .	—	—	1·24
Ammonium sulphate . . . . .	—	—	0·54
Silica . . . . .	—	—	2·20

The soot from the condensing chamber of the shaft furnace No. IX., collected in 1892, had the following composition :—<sup>2</sup>

Metallic mercury . . . . .	65·04 = 65·04 Hg
Mercuric sulphide . . . . .	6·97 = 6·0
Basic mercuric sulphate . . . . .	0·20 = 0·16
Mercuric sulphate . . . . .	0·12 = 0·08
Mercuric chloride . . . . .	0·08 = 0·06
Mercurous chloride . . . . .	0·05 = 0·04

71·38 per cent. Hg.

<sup>1</sup> Das k. k. Quecksilberbergwerk Idria, Vienna, 1891.

<sup>2</sup> Janda, Oesterr. Zeitschr., 1894, p. 268

Alumina and ferric oxide . . . . .	1·11
Ferrous sulphide . . . . .	0·94
Lime . . . . .	9·57
Magnesia . . . . .	0·40
Sulphur trioxide . . . . .	9·10
Ammonia } . . . . .	2·19
Hydrocarbons } . . . . .	
Soot . . . . .	1·98
Silica . . . . .	1·20

In 1892, samples of soot were taken at various places along the course which the gases and vapours traversed through the furnace until they reached the stack delivering them into the atmosphere, and were examined for their contents of moisture and mercury. The results of the analyses are shown in the following table. In this No. 1 was taken from the flue of the shaft furnace, Nos. 2 and 3 from the condensing chamber of the Czermak furnaces, No. 4 from the flue of one of the Czermak furnaces, Nos. 5 and 6 from the flue leading to the fan, and Nos. 7 and 8 from the main stack :—

Number of the sample.	Moisture per cent.	Percentage of mercury as			Total Mercury per cent.
		Salts.	Cinnabar.	Metal.	
1 . . . . .	14·8	0·20	18·83	43·17	62·20
2 . . . . .	—	3·04	6·75	22·01	31·80
3 . . . . .	85·8	trace	4·00	18·00	22·00
4 . . . . .	40·2	—	6·40	21·80	28·20
5 . . . . .	—	0·16	9·68	3·76	13·60
6 . . . . .	—	0·75	9·24	4·16	14·15
7 . . . . .	35·0	0·69	13·75	0·86	15·30
8 . . . . .	65·9	0·16	9·35	3·49	13·00

The proportion of mercury respectively contained by the salts, cinnabar, and metal of the various samples was therefore distributed as follows :—

Number of the sample.	Percentage of the total mercury present in the form of		
	Salts.	Cinnabar.	Metal.
1 . . . . .	0·32	30·28	69·40
2 . . . . .	9·55	21·23	69·22
3 . . . . .	trace	18·18	81·81
4 . . . . .	—	22·69	77·30
5 . . . . .	1·17	71·18	27·65
6 . . . . .	5·30	65·30	29·40
7 . . . . .	4·51	89·87	5·62
8 . . . . .	1·23	71·92	26·84

Soot from Almaden has the following composition :—<sup>1</sup>

	Soot from clay condensing tubes. Per cent.	Soot from iron condensing tubes. Per cent.
Mercury as metal . . . . .	66	44
Mercurous chloride . . . . .	18	3.3
Mercuric sulphide . . . . .	1	6.3
Ferrous sulphate . . . . .	—	23.5
Aluminium sulphate } . . . . .	—	14.5
Potassium sulphate }		
Ammonium sulphate . . . . .	3.5	—
Calcium sulphate . . . . .	1	0.9
Carbon . . . . .	5	4.8
Sulphuric acid . . . . .	2.5	—
Water . . . . .	2.5	—

### *The Treatment of Soot*

Mercury is extracted from soot, firstly by *pressing* the latter, whereby a considerable portion (up to 90 per cent) of mercury is made to flow out, and secondly, by treating the residues thus obtained, either together with ores or by themselves, in distillation furnaces. Experiments made in Idria by Czermak and Spirek with the object of extracting the quicksilver by burning the soot, after previously pressing it, have given unsatisfactory results due to the high loss of metal entailed. Soot is pressed either by hand or by machinery. To promote the removal of the mercury, lime or ashes are added to it. The best method of pressing soot consists in treating it in pans or cylinders, provided with stirrers, which on a large scale are driven by machinery.

At Almaden,<sup>2</sup> the soot is worked upon an inclined wooden surface with hoes until no more mercury flows off. The residues are then moulded into bricks and treated with the ores. The rubbing up of soot in this way was also carried on at Idria and in the Californian Works, but on account of its being injurious to the health of the workmen has been given up for a considerable time. For example, at the Redington Mine in California,<sup>3</sup> soot was treated in this way, the residues being heated in retorts with lime. At New Almaden the soot was first treated as above.<sup>4</sup> As soon as no more mercury could be extracted in this way, lime was added and the rubbing continued, when another portion of mercury was obtained.

At Idria, the soot presses designed by Exeli are at present employed. Their construction is shown in Figs. 378 and 379. They consist of iron cylinders with a V-shaped bottom. The diameter of the cylinder in the clear amounts to 4 feet, the height to 17 inches.

<sup>1</sup> *Berg- und Hüttenm. Jahrb. der k. k. Montanlehranstalten, Vienna, 1879, p. 81*

<sup>2</sup> *Ibid.*, vol. xxvii., p. 46.

<sup>3</sup> *Egleston, op. cit.*, p. 850.

<sup>4</sup> *Egleston, op. cit.*, p. 834.

Through the middle of the cylinder passes a vertical shaft *w*, to the upper end of which are attached four arms at right angles to each other, these arms being  $11\frac{1}{2}$  inches above the bottom of the apparatus. To these arms are bolted knives *z*, 3 inches broad and 0.3 to 0.4 inch thick. To the bottom of the apparatus seven or eight vertical knives, *o*, of the same dimensions, are so attached that when the arms revolve the movable knives *z* pass close to the fixed knives, and thus press the soot together and force it upwards. In the lowest portion of the apparatus there are 25 apertures of 0.4 inch diameter, through which the mercury flows away as fast as it is pressed out. These openings readily become stopped up, and must be kept open during the operation by means of a stout wire. It is important that the bottom ends of the movable knives should touch

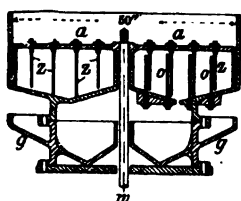


FIG. 378.

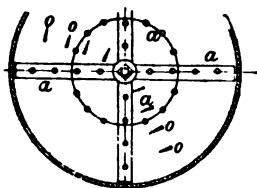


FIG. 379.

the bottom of the apparatus, and when they are worn they should be immediately replaced by new ones, otherwise a layer of soot forms upon the bottom of the apparatus which stops up the holes through which the mercury should escape. When the shaft is set in motion the mercury is squeezed out from the soot mixed with lime, and collects in the lowest portion of the bottom, whence it runs through the above-named openings into the receiver *g* standing beneath it. The soot residues are also collected in a box placed beneath the apparatus. The weight of a charge of soot depends upon the amount of mercury and of moisture contained in it, and varies between 44 and 110 lb. The quantity of lime to be added depends upon the same conditions. More must be added to soot rich in mercury than to poor soot, the amount varying between 17 and 30 per cent. of the weight of the soot; the lime is not added all at once, but in small quantities during the course of the operation. The speed of revolution is at first low, and rises gradually from 12 to 40 revolutions per minute. After 20 minutes the knives ought to commence to lift the soot from the bottom of the apparatus and to throw it up. Generally speaking, the soot is sufficiently well pressed when the residues begin to agglomerate into pellets. The time required for pressing depends upon the richness of the soot. In the case of rich material it lasts

from  $1\frac{1}{2}$  to  $1\frac{3}{4}$  hour. By this operation from 70 to 80 per cent. of the mercury contained in the soot is separated, the remainder of the mercury, which amounts on the average to 14 to 20 per cent. of the weight of the residues, being obtained by distilling these residues together with ores. A sample of pressed soot from shaft furnace No. VIII., taken in December, 1892, contained :—<sup>1</sup>

	Per cent.
Mercury in combinations soluble in hydrochloric acid . . . . .	0.17
Mercury as cinnabar . . . . .	2.96
Metallic mercury . . . . .	14.98
	—
Total . . . . .	18.11
	—

At the works in Monte Amiata, the pressing is carried out in appliances similar to the Exeli press, the output of quicksilver from the soot there treated being 80 to 90 per cent.

At New Almaden, the soot was treated from 1873 to 1887<sup>2</sup> in hemispherical cast-iron pans 36 inches in diameter, for three-quarters of an hour, by constant stirring with boiling water and wood ashes. The quantity of the latter amounted to half of the volume of the soot. The quicksilver that separated out was drawn off from the bottom of the pan by means of a syphon. The residues were dried and treated together with the ores in distillation furnaces.

A cast-iron pan was also employed at the Manhattan Works. Above the pan, of a capacity of 120 gallons, a vertical shaft was carried by a wooden frame. To the bottom end of the former horizontal wooden arms were attached carrying iron tines. The soot was mixed with ashes and lime, and the mass was stirred for 20 minutes, at the end of which time all the mercury that could thus be removed had been extracted, and the mass was completely dry. The mercury was drawn off by means of a pipe at the bottom of the pan and the residues were distilled in retorts.

Lukasiewicz<sup>3</sup> presses the soot, without the addition of other bodies, in a vacuum at a temperature of 30° to 90° C. The combination of reduced pressure and gentle warming dries the soot, and drives off the volatile oils contained in it without an appreciable loss of mercury; furthermore, as the operation is carried out in closed vessels, the health of the workmen is not affected. The apparatus consists of a double-walled cast-iron pot fitted with rollers and connected by a pipe with the vacuum supply. The pot is heated out-

<sup>1</sup> Janda, *op. cit.*, p. 269.

<sup>2</sup> Egleston, *op. cit.*, p. 884.

<sup>3</sup> Austrian Pat. No. 11,689.



side by a fire or by steam, and water circulates between its walls. The soot is fed in through two manholes in the upper part of the pot, and the rollers are movable along an upright shaft that reaches to the bottom of the pot. The charge varies from 6,600 to 27,600 lb. of soot. The upper surface of this is pressed by two grooved rollers which slip down the shaft under their own weight as the charge contracts owing to loss of mercury and evaporation of oil and water. This continues until all the available quicksilver has been squeezed out. The mercury escapes through two holes in the bottom of the pot. The shaft is square in section, and makes 20 to 30 revolutions a minute. With this apparatus it is stated that up to 95 per cent. of the quicksilver in the soot may be extracted. It is in use with excellent results at Kotterbach, Zips, Hungary.

At present, at New Almaden, wet and semi-fluid<sup>1</sup> soot is stiffened by mixing with half its volume of wood ashes upon a rectangular asphalted floor, 20 feet long and 9 feet broad, which is hollowed and at the same time inclined to one of its shorter sides; a paste is thus obtained which is transferred in buckets to the press, consisting of a cast-iron pan of 40 inches diameter at its upper wider end. In it there stands a vertical shaft with four plough-shaped stirrers. The mass is stirred for  $1\frac{1}{2}$  hour, the stirrers making 40 revolutions per minute, at the end of which time no more mercury flows out. The mercury is drawn off by means of a syphon at the bottom of the pan. The residues are drawn off into a box standing below the pan, through a larger opening in the bottom of the pan, which is kept closed during the course of the operation by means of a valve, 14 per cent. of the mercury contained in the soot remains in the residues, which are treated by distillation; it is impossible to remove the whole of the mercury from the soot by pressing alone.

The residues contain, according to the method of pressing employed, variable quantities up to 40 per cent. of mercury. For example, in Idria<sup>2</sup> the residues obtained by pressing in the years 1890 to 1892 contained 14.89 per cent. of the entire output of mercury. In order to extract this mercury from the residues, the latter must therefore be subjected to a further treatment. This consists in distilling the residues in the same way as the ores in the various furnaces used for ore treatment, as a general rule mixed with ore, and more rarely by themselves. At Almaden the soot residues are moulded into bricks and are treated with the ores. At Idria, the residues were treated for a while in retort furnaces; now, however, they are distilled with the ores in shaft and reverberatory furnaces. When soot residues were distilled in retort furnaces, a resinous substance, known as "soot

<sup>1</sup> Egleston, *op.cit.*, p. 882.

<sup>2</sup> Mitter, *loc. cit.*

fat" (*Stuppfett*), condensed in the receivers; it consisted chiefly of hydrocarbons mixed with only small quantities of mineral substances. According to G. Goldschmidt and M. von Schmidt, 32 kilos. of *Stuppfett* only contained 150 grammes of mineral matter, which latter contained 70·35 per cent. of mercury, partly as metal, partly in combination with sulphur together with iron, manganese, alumina, lime, and magnesia. Since the use of muffle furnaces has been discontinued in the year 1892, no more of this *Stuppfett* has been produced. For treatment in shaft furnaces at Idria, the soot from the condensing chambers of the flues, together with the residues of the furnace soot, were mixed with ground clay, pressed and moulded into lumps, which were treated together with poor coarse ore. The coal was mixed with a certain quantity of coke. Further quantities of residues were treated in the Czermak furnaces and in the reverberatory furnaces. At Monte Amiata the residues were formerly treated in muffles, now, however, in small Spirek furnaces. In California the residues are worked either by themselves in retorts or together with the ores in the furnace, together with the ores suitable for treatment in these furnaces suitable to the various grades. In New Almaden, in the year 1888, 18 per cent. of the total mercury production was obtained from soot. Recently at Idria, of the total production of mercury, including a loss of 9 per cent., 56 per cent. was obtained by pressing the soot and 15 per cent. by distillation of the soot residues.

The acid water from the condensers contains sulphuric and sulphurous acids, sulphates of iron, mercury, calcium, and ammonia. hydrocarbons, and in some cases small quantities of hydrochloric acid and floured mercury. According to Janda,<sup>1</sup> the acid water condensed in the year 1892 at Idria in the condenser of shaft furnace No. X. had the following composition:—

	Per cent.
Hg <sub>2</sub> O . . . . .	0·33
FeO . . . . .	14·38
CaO . . . . .	0·50
SO <sub>3</sub> . . . . .	11·01
SO <sub>2</sub> . . . . .	1·97
NH <sub>3</sub> . . . . .	0·61
HCl . . . . .	0·06
Condensable hydrocarbons, including the acetic acid series . . . . .	22·12
Water and undetermined . . . . .	48·12

The specific gravity of this water was 1·65 at 15° C. If the acid water contains floured mercury, as is, for instance, the case at New Almaden, it is freed from it by filtration through charcoal. The

<sup>1</sup> Oesterr. Zeitschr., 1894, p. 270.

water runs off clear, leaving a black slime upon the filter. The latter is dried and is then distilled, together with the ores.

*Distillation Residues.* When the operation is carried out properly the residues are so poor in mercury that they can be thrown away. For example, the residues from the Idrian shaft furnace contained in 1877<sup>1</sup> 0·002 per cent. of mercury, and those from the reverberatory furnaces<sup>2</sup> contained 0·006 per cent. in 1877, 0·0001 per cent. in 1879, and in 1892 only traces of mercury.

### *The General Arrangement of a Mercury Works*

As an example of the general arrangement of a quicksilver works with modern furnaces, condensers, and fan, the plant at Idria may be described. The ores there average upon the whole 0·5 to 0·8 per cent. of mercury. The ores were formerly divided into slimes, fine ore, coarser ore, and lump ore, but now the four following divisions are made:—

1. *Reicher Erzgries*.—"Rich small ore" with about 6 per cent. of mercury. This is divided into two classes: (1) of 0·16 to 0·32 inch mesh, and (2) below 0·16 inch. Both grades are again subdivided into those containing more than 10 per cent. and those containing less than 10 per cent. of mercury.

2. *Armer Erzgries prima*.—"Poor small ore of first quality," containing 0·7 per cent. of mercury and less than 0·8 inch in size.

3. *Armer Erzgries secunda*.—"Poor small ore of second quality," containing 0·4 per cent. of mercury and 0·8 to 1·2 inch in size.

4. *Armer Erzgröb*.—"Poor coarse ore," containing 0·3 per cent. of mercury and 1·2 to 4 inches in size.

The complete analyses of the various grades of ore were as follows in the year 1881:—<sup>3</sup>

	Slimes.	Fine ore.	Coarse ore.
	Per cent.	Per cent.	Per cent.
Mercuric sulphide . . . . .	0·62	1·25	8·58
Mercurous chloride . . . . .	trace	trace	0·22
Basic mercuric sulphate . . . . .	—	—	trace
Ferrous carbonate . . . . .	0·76	3·17	4·27
Calcium carbonate . . . . .	35·75	27·21	14·71
Calcium sulphate . . . . .	0·53	1·46	2·42
Magnesium carbonate . . . . .	27·17	20·33	4·20
Magnesium sulphate . . . . .	0·21	0·55	1·11
Iron bi-sulphide . . . . .	4·24	4·31	5·09
Alumina . . . . .	1·64	1·61	1·30
Phosphoric acid . . . . .	—	—	trace
Aluminium silicate . . . . .	16·48	22·75	15·82
Ferrous silicate . . . . .	—	trace	20·18
Silica . . . . .	11·52	16·48	17·64
Bitumen . . . . .	1·08	1·63	3·97
Water and loss . . . . .	—	—	0·49

<sup>1</sup> *Idrianer Festschrift.*

<sup>2</sup> *Ibid.*

<sup>3</sup> *Ibid.*, Vienna, 1881.

The composition in 1892<sup>1</sup> was the following:—

	Rich small ore.	Poor small ore.	Poor coarse ore.
	Per cent.	Per cent.	Per cent.
HgS . . . . .	6·74	0·95	0·38
FeS <sub>2</sub> . . . . .	9·49	11·64	4·45
FeCO <sub>3</sub> . . . . .	2·52	6·66	4·76
CaCO <sub>3</sub> . . . . .	26·18	27·13	34·86
MgCO <sub>3</sub> . . . . .	16·69	10·24	24·92
CaSO <sub>4</sub> . . . . .	1·05	2·93	0·79
MgSO <sub>4</sub> . . . . .	0·44	0·74	0·32
Ca <sub>3</sub> P <sub>2</sub> O <sub>8</sub> . . . . .	0·75	0·41	0·32
Al <sub>2</sub> O <sub>3</sub> (amorphous) . . . . .	2·60	4·80	3·53
SiO <sub>2</sub> . . . . .	30·04	31·77	23·82
Bitumen . . . . .	0·97	0·70	0·62
Organic matter and water of crystallisation . . . . .	2·53	2·03	1·17
Cl. . . . .	distinct trace	—	—

The ores are treated by heating them with access of air in the furnaces already described. The rich small ore is treated in the Czermak furnace, the poor small ore of first quality in Czermak furnaces and long-bedded calciners, the poor small ore of second quality and the poor coarse ore in shaft furnaces. The works contain three Czermak furnaces, eight long-bedded calciners, and nine shaft furnaces. The practical results obtained, which have already been set forth under the heads of the various individual furnaces, together with the annual mercury production of the furnaces, is shown in the following table of the results obtained in the year 1892:—

Class of furnace.	Grades of material treated.	Amount treated per day per furnace.	Wages.		Fuel consumption per 10 tons of ore.	Soot production.	Mercury produced.
			Per 10 tons of ore.	Per 100 kilos (3 cwt.) of mercury.			
Novak shaft furnaces . . . . .	Poor coarse ore and soot . . . . .	Tons. 12·15	s. d. 13 4	s. d. 42 1	58·3 charcoal	0·5	109
Czermak furnace, No. 1 . . . . .	Poor and rich small ore and soot . . . . .	22·46	17 9	5 10	130·7 wood	3·3	244
Czermak furnaces, Nos. 2 and 3 . . . . .	Poor small ore and soot . . . . .	26·75	14 0	19 1	106·6 „	1·3	117
Calciners, Nos. 1 to 6 . . . . .	Poor small ore and soot . . . . .	6·6	21 6	29 9	148·9 „	1·9	71
Calciners, Nos. 7 and 8 . . . . .	Residues from old Leopoldi furnaces and soot . . . . .	6·85	23 10	119 5	156·5 „	2·0	81

<sup>1</sup> Janda, *Oesterr. Zeitschr.*, 1894, p. 267.

The temperature at which the gases and vapours escape from the various furnaces<sup>1</sup> is, upon the average:—

Long-bedded calciners . . . . .	341° C
Czermak furnaces . . . . .	353° C
Shaft furnaces . . . . .	226 to 233° C.

The quicksilver is condensed in Y-shaped pipes of earthenware and small wooden flues connected with these. The latter are connected by flues with underground central chambers common to all the furnaces, and communicating with the fan which draws the gases into the long stack-flue.

In Fig. 380 a general ground plan of the works is given, showing the connection of the furnaces with the condensers, the mode of communication of the various condensers with the underground central condensing chambers, and the connection of the latter with the fans. The draught was first produced by a stack alone, and then by means of a furnace connected with the stack, but recently fans have been employed for this purpose. They are found to have an especially good effect upon the general mode of working, the health of the men engaged, and the diminution of the losses of mercury. There are two fans, one of which is in reserve. The fans were first made of cast-iron, then of varnished sheet-iron, and finally of sheet-brass. All these materials have, however, at present been replaced by others, the disc of the fan now consisting of brass, whilst the vanes are made of sheet-copper; the diameter of the fan is 8 feet and its speed is between 189 and 280 revolutions per minute, producing a normal depression of 0·7 inch water-gauge. The cubical contents of the various condensers and flues is shown in the following table:—

	Volume of Condensers.		
	Chambers.	Flues.	Total.
	Cubic feet.	Cubic feet.	Cubic feet.
Shaft furnaces . . . . .	33,568	6,569	40,137
Czermak furnaces . . . . .	35,916	2,013	37,929
Calciners 1 to 6 . . . . .	50,148	706	50,854
Calciners 7 and 8 . . . . .	3,885	742	4,627

<sup>1</sup> Janda, *Oesterr. Zeitschr.*, 1894, p. 298.

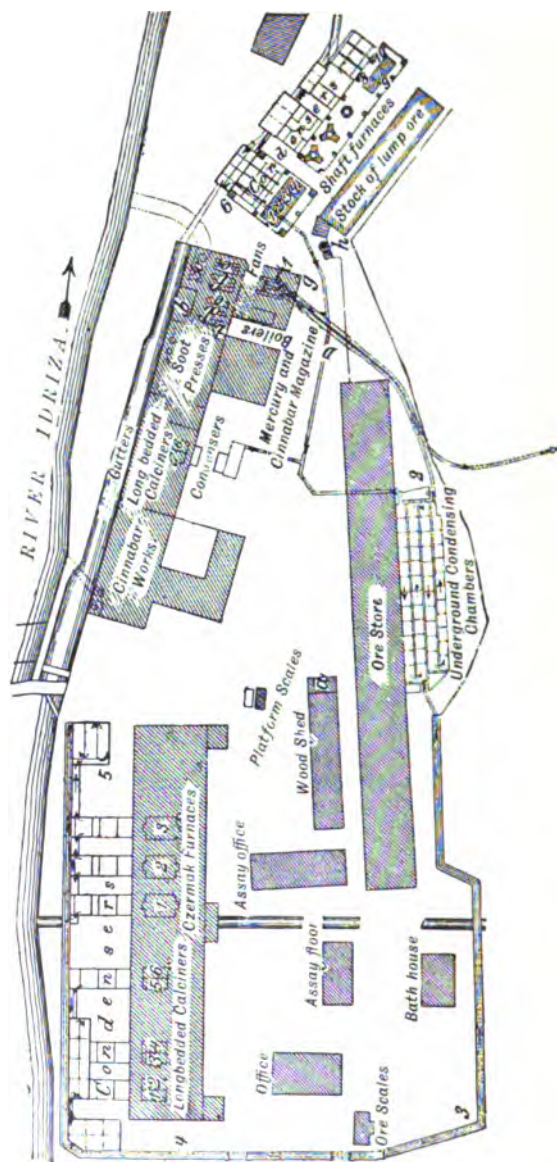


FIG. 380.

To these must be added the space common to all the furnaces, viz :—

	Chambers.	Flues.	Total.
	Cubic feet.	Cubic feet.	Cubic feet.
Underground central chambers .	63,085	—	63,285
Flues connecting the calciners and Czermak furnaces above ground	—	20,236	20,236
Flue from the central chamber to the fan . . . . .	—	4,944	4,944
Flue from the fan to the stack . .	—	18,576	18,576

The total contents of the condensing appliances therefore amount to :—

Chambers . . . . .	186,802 cubic feet
Flues . . . . .	53,786 „ „
<b>Total . . . . .</b>	<b>240,588 „ „</b>

The gases and vapours from the shaft furnaces enter the condenser at a temperature of 114° C., and leave it at 15° C.; those from the Czermak furnaces enter with a temperature of 109° to 180° C., and escape at 21° to 30° C.; those from the calciners enter at 174° C. and escape at 25° C. According to Mitter, the average of the mercury extracted in the years 1890 to 1892 was obtained :—

	Per cent.
From the condensers and from pressing the soot. .	74·64
From the residues of the soot . . . . .	14·89
From the soot collected in the more remote flues and chambers . . . . .	5·22
The loss of mercury was . . . . .	8·25

According to recent communications from Mitter, in Idria the extraction of mercury is at present distributed as follows :—

	Per cent.
No. 1. Metallic mercury taken direct from the condensers. . . . .	20
No. 2. Obtained by pressing the soot . . . . .	56
No. 3. Obtained by treatment of the soot residues . . . . .	(about) 15
The loss of mercury being about . . . . .	9

*Nikitovka, Russia*<sup>1</sup>

These works were started on a working scale in 1886 to treat cinnabar ores from the Carboniferous formation. These ores contain on the average 0.75 per cent. of mercury. They are broken in rock breakers and dropped on to a picking belt, on which about 16 per cent. of barren rock is picked out. Lump ores in sizes up to that of twice a man's fist are treated in barrel-shaped furnaces of 16 feet 6 inches in height and 11 feet 6 inches in diameter in the widest part, the ore being mixed with coal. The condensing appliances consist of Y-shaped pipes made of cast-iron lined with cement. The small ore and the dust from the dressing works, which is rich in mercury, together with the soot residues, are treated in furnaces similar to the Idrian Czermak furnaces already described, four of which form one block. The condensers are similar to those already described. The soot is treated in rotating barrels with lime, whereby the greater portion of its mercury is extracted. The output of mercury from the ores is given as 0.563 per cent., the loss of mercury during treatment at 12 per cent.

## THE EXTRACTION OF MERCURY FROM MERCURIAL FAHLORES

Mercury is obtained as a bye-product during the calcination of mercurial fahlores. The author has seen mercury obtained in this way at the Stefan Works, near Göllntz, in Upper Hungary. Antimonial fahlore, containing 30 to 39 per cent. of copper, 25 to 33 per cent. of antimony, 0.10 to 0.12 per cent. of silver, and 0.52 to 1.7 per cent. of mercury, with an average content of 1.63 per cent. of mercury, is retreated in circular stalls, 23 feet in diameter and 6 feet 6 inches high, which are covered over. These stalls, the lower portion of which is provided with draught-holes for the admission of air, contain 67 to 70 tons ore. The ores are piled upon a bed of cord-wood; layers of wood are also introduced between the ores in such a way that spaces are produced, which become filled with charcoal, and, after the latter is burned, serve as air flues. During the calcination of the ore, the mercury is evolved in the metallic state and is condensed in the topmost layers of ore. When the latter, in the course of continued calcination, get heated, fresh ore is piled on, into which the mercury is then driven, and where it condenses. After the completion of the calcination, which lasts three to four weeks, the upper layers of ore are taken off and washed in type

<sup>1</sup> *Russian Mining Journal (Gorni Journal)*, 1891, No. 20.



for the extraction of the mercury. The mercury obtained is distilled in iron retorts and then packed in sheepskin bags. The residues from washing and from distillation are treated for copper and silver. With such a process the loss of mercury by its escape into the air, the sides and the floor of the stalls, is unavoidable. Modern apparatus for the extraction of mercury from fahlores is at present in operation at Josephi, near Kotterbach, Upper Hungary. The ores are sorted into lump fahlore, of 0·2 and 1·2 inch mesh, and mixed fahlore and heavy spar from the washery. The composition of these ores is as follows.

	Sorted ore.	Washed ore.
Sulphur . . . . .	7·97	1·26
Mercury . . . . .	1·85	0·50
Copper . . . . .	9·75	1·38
Antimony . . . . .	3·03	0·80
Arsenic . . . . .	0·17	—
Silver . . . . .	0·02	—
Ferrous oxide . . . . .	42·75	14·17
Manganous oxide . . . . .	1·69	0·69
Lime . . . . .	0·42	0·35
Magnesia . . . . .	3·97	1·32
Carbon dioxide . . . . .	24·23	8·65
<i>Insoluble.</i>		
Silica . . . . .	3·73	1·27
Ferric acid . . . . .	0·57	6·46
Magnesia . . . . .	0·26	1·07
Barium sulphate . . . . .	—	67·15

The constituent compounds are given as follows:—

$\text{Cu}_2\text{S}$ . . . . .	12·22	$\text{As}_2\text{S}_3$ . . . . .	0·20
$\text{Ag}_2\text{S}$ . . . . .	0·02	$\text{FeCO}_3$ . . . . .	53·91
$\text{HgS}$ . . . . .	2·15	$\text{MnCO}_3$ . . . . .	2·97
$\text{FeS}$ . . . . .	11·00	$\text{MgCO}_3$ . . . . .	13·89
$\text{Sb}_2\text{S}_3$ . . . . .	4·24		

The ores are roasted in a Czermak furnace, 12,000 lb. being worked off in 24 hours with a fuel consumption of 120 cubic feet of wood. The vapours leave the furnace at a temperature of 350—360° C, and pass into Czermak condensers made of earthenware and connected with chambers and flues. The condenser pipes are cooled on the outside by running water and the ends dip two inches deep into water which is contained in iron tanks lined with cement. The product of condensation is soot alone, and this on pressing gives 49·51 per cent. of quicksilver and 50·49 per cent. of mud containing 60·25 per cent. of mercury and 4·21 per cent. of mercuric oxide. Pressing is performed in Exeli presses and in those of Lukasiewicz. The press residues are treated in Czermak furnaces; the distillation residues still contain 0·04 per cent. of mercury. The calcined ores which contain 11·72 per cent. of copper and 0·025 per cent. of silver are melted at the copper works at Witkowitz.

## EXTRACTION OF MERCURY FROM METALLURGICAL PRODUCTS

The chief metallurgical products containing mercury are soot and the amalgams obtained in the course of gold and silver extraction. The process of soot treatment has already been described. The extraction of mercury from gold and silver amalgams when these metals are obtained by amalgamation has been fully considered in Volume I., pages 842 and 972. Mercury is also obtained in small quantities from the flue-dust resulting from the calcination of blende rich in mercury, as also from the slimes of the lead chambers, in which the sulphur dioxide evolved on calcining these blendes is converted into sulphuric acid. The Swedish blende calcined at Oberhausen contains 0·2 per cent. of mercury, according to Bellingrodt.<sup>1</sup> The flue-dust which is deposited during the calcination in the dust chambers nearest the calcining furnace contains 6 to 7 per cent. of mercury, the slimes of the lead chambers into which the products of calcination are conducted 4 per cent. of mercury. Both these bye-products are treated for the mercury they contain. The mode of treatment is not mentioned, but it is probably by distillation.

Fairly large quantities of quicksilver are won at Kotterbach in Upper Hungary from the gases evolved during the calcination of spathic iron ore containing small amounts of mercurial fahlores.<sup>2</sup> The ores for calcination are mixed so as to contain on the average :—

Soluble part.				Insoluble part.	
FeCO <sub>3</sub> . . .	74·59	Cu <sub>2</sub> S . . .	0·57	SiO <sub>2</sub> . . .	3·17
Fe <sub>2</sub> O <sub>3</sub> . . .	3·32	FeS <sub>2</sub> . . .	0·78	Al <sub>2</sub> O <sub>3</sub> . . .	0·85
Al <sub>2</sub> O <sub>3</sub> . . .	0·35	Sb <sub>2</sub> S <sub>3</sub> . . .	trace	Fe <sub>2</sub> O <sub>3</sub> . . .	
MnCO <sub>3</sub> . . .	3·59	As <sub>2</sub> S <sub>3</sub> . . .			
MgCO <sub>3</sub> . . .	11·61	BaSO <sub>4</sub> . . .	0·64		
		HgS . . .	0·11		
Organic matter and water, 0·65					

The calcination is carried out in shaft furnaces, and the gases produced, which were formerly drawn from the main flue by means of Körting injectors with clay nozzles, are now extracted by fans and led through cast-iron and clay flues into towers made of two-inch larch planks. Two towers are combined in a block. The joints of the towers are caulked with hemp and a mixture of kaolin, tar, and varnish. Inside of each tower are two grids heaped up with lumps

<sup>1</sup> *Chem. Ztg.* 1886, No. 68.

<sup>2</sup> *Verhandlungen d. Vereins zur Beförderung des Gewerbfleisses*, 1899, vol. v. p. 185 to 209, vol. vi. and vii. p. 246.

of limestone, over which water trickles in a constant stream. The furnace gases enter at the foot of the first tower, rise up through the grid and between the stones, are drawn downwards through wooden flues (formerly earthenware pipes were used), and traverse the second tower in like manner, escaping at the top into the open air. The water from the towers was formerly run direct into a system of six settling tanks where the suspended matter separated out as mud, and the supernatant liquor was run into the wash-waters from the ore dressing, so that its sulphur dioxide contents was rendered innocuous. The quicksilver present in the furnace gases is precipitated partly in the flues and partly in the tower liquors, being present as dust containing 9·8 per cent. of mercuric oxide in the flues in front of the injector or fan, and as a grey mud containing 5·85 per cent. of mercuric oxide in the flues behind the fan. The mud which collects in the settling tanks contains 6·60 per cent. of mercuric oxide. The water from the first tower contains 1·5 grains per gallon of quicksilver, that from the second tower contains 1 grain per gallon. The mercury contained in the waste waters used to be precipitated with residues containing soda. At present the liquors condensed in the flues and those from the towers are filtered through sulphite filters and ordinary charcoal filters, and are freed thereby from all but traces of mercury. All the products containing quicksilver which are obtained in this way from the furnace gases are treated along with mercurial fahlores and soot at the works at Kotterbach.

#### THE EXTRACTION OF MERCURY IN THE WET WAY

The extraction of mercury in the wet way has been repeatedly proposed, but has not yet been introduced, nor is there any prospect of its introduction. Sieveking<sup>1</sup> proposes to treat ores containing cinnabar with a solution of cuprous chloride in salt in the presence of a granulated alloy of copper and zinc in revolving barrels. Cinnabar is thereby decomposed with the liberation of mercury and the formation of cupric sulphide and cupric chloride, as shown by the equation:—



Metallic mercury amalgamates with the copper-zinc alloy, and can be removed from the latter by distillation. Alkaline sulphides containing caustic alkalies (see page 332) also gave unfavourable results as also did the use of cupric chloride. Solutions of bromine in water and of bromine in concentrated hydrochloric acid, which had been

<sup>1</sup> *Oesterr. Zeitschr.*, 1876, No. 2; *Berg- und Hüttenm. Ztg.*, 1876, p. 161.

proposed by R. Wagner,<sup>1</sup> have not come into use. Mercury can be extracted from substances containing mercurous chloride by solutions of hyposulphites.

### *The Electrolytic Extraction of Mercury*

No attempts have yet been made to extract mercury electrolytically. In view of the simplicity of the dry methods of mercury extraction, it is doubtful whether the electrolytic method, admitting even its possibility in the case of poor ores, would prove more advantageous than the dry method, in spite of the losses in the latter. It must, however, be admitted that cinnabar is readily soluble in solutions of alkaline sulphides containing caustic alkalies, and that the electrolysis of the solutions of mercury sulphide and oxide thus obtained should offer no difficulties, and would not require any very high electric tension.

According to Brand,<sup>2</sup> cinnabar is readily decomposed at the anode of an electric circuit, whilst mercury is thrown down at the cathode, a solution of common salt or dilute hydrochloric acid being employed as a bath. The tension in the bath is said to amount to 1 volt. The power to extract 1 kilogram of mercury in this way would accordingly amount to

$$\frac{1 \text{ volt} \times 266.5 \text{ ampères}}{650 \text{ watts} \times 0.75} = 0.54 \text{ horse-power per hour,}$$

since 266.5 ampères can deposit 1 kilogram of mercury per hour and since one horse-power, assuming 12 per cent. of loss in conversion, would yield not 735, but 650 watts, and since the loss of current by conversion into heat, by short-circuiting, &c., amounts to 25 per cent. As 2 kilogram of coal would be required per horse-power per hour, the coal consumption per kilogram of mercury would come out at 1.08 kilogram. With the most modern steam engines, the loss of power in the conversion of mechanical work into electrical energy amounts to 9 per cent., and in the dynamo to 6 per cent., making a total of 15 per cent., whilst the loss of current in the conductors may be taken as 10 per cent., and the consumption of coal in the best steam engines amounts to 1 to 1.5 kilogram per horse-power per hour. A. v. Siemens<sup>3</sup> proposes to convert mercuric sulphide (like the sulphide of antimony and arsenic) into a soluble double sulphide by treatment with sulph-hydrates of calcium, barium, strontium, or magnesium, and to electrolyse this without diaphragms.

<sup>1</sup> *Dingler*, vol. cxxviii., p. 254; *Chem. Centralblatt*, 1878, p. 711.

<sup>2</sup> Dammer, *Chem. Technologie*, vol. ii. p. 41.

<sup>3</sup> Eng. Pat. No 7123, April 1, 1896.

In this way the hydrogen liberated at the cathode combines with the sulphur of the mercuric sulphide, setting free mercury and forming the sulph-hydrates of calcium, barium, strontium, and magnesium, which latter are then converted into bisulphides by the oxygen evolved during the electrolysis. The bisulphides may then be treated with carbon dioxide, when sulphuretted hydrogen will be evolved and the metals thrown down as carbonates mixed with sulphur. This mixture heated out of contact with air yields sulphur, carbon dioxide, and the oxides of the earthy metals; of these products the carbon dioxide may be used to decompose fresh bisulphide solutions, and the sulphur and the oxides of the metals may be converted into fresh sulph-hydrates. This process has not found practical application.

#### THE MANUFACTURE OF ARTIFICIAL CINNABAR

At many works a portion of the mercury extracted is converted into artificial cinnabar, as, for instance, at Idria in Carniola. A short account of the preparation of cinnabar at this place, as far as it is not kept secret, will accordingly be given. Artificial cinnabar can be produced both in the dry and wet way. In the dry way the sulphur is combined directly with mercury. For the production of cinnabar in the wet way metallic mercury or compounds of mercury, together with sulphur, are treated with solutions of caustic soda or potash, with potassium or sodium polysulphides, with ammonium sulphide or with sodium hyposulphite at suitable temperatures. Processes for the production of cinnabar in the wet way have, for example, been devised by Kirchhoff, Brunner, Firmenich, Liebig, Martens, Fleck, Gautier-Bouchard, Haussmann, and Jean Maire. At Idria cinnabar has been produced in the dry way for a long time. Since 1880 it has also been manufactured in the wet way successfully; nothing, however, can be said about the latter process, as it is kept secret.

Cinnabar is produced in the dry way at Idria by mixing together mercury and sulphur in revolving barrels, heating the mixture produced in iron retorts so as to complete the combination of sulphur with mercury, volatilising the excess of sulphur, and finally subliming the cinnabar thus formed, which is then ground and refined by being boiled with a solution of potash. The first operation, or the mixing of sulphur and mercury, is known as amalgamation or the preparation of the "*Moor*." The second operation, or heating the mixture in retorts, is known as subliming the *Moor*, or the production of lump cinnabar. The third operation, grinding the lump cinnabar; and the last, the refining of cinnabar. The first

operation consists in mixing pounded sulphur, which is passed through a sieve of  $\frac{3}{4}$ -inch mesh, with mercury in small horizontal rotating casks made of elm, with internal projecting ridges. 16 parts of sulphur are added to 84 parts of mercury; the charge for a barrel amounts to 55 lb. The barrels make 60 revolutions per minute, 30 to the right and 30 to the left. After two or three hours' treatment, the black mass thus produced, known as the crude *Moor*, is removed from the barrels and submitted to the second operation. The second operation, or sublimation, is performed in cast-iron, pear-shaped retorts, each of which holds 114 lb. of *Moor*. There are six of these retorts in a reverberatory furnace heated with wood. Three stages are distinguished in this operation, viz. *Abdamfen* ("boiling off"), *Stücken* ("forming lumps"), and *Sublimiren* ("sublimation"). In the first stage the combination of sulphur and mercury is completed; the retorts are covered with hoods of sheet-iron, the necks of which point upwards and project from the arch of the furnace. The heat is raised slowly, and in fifteen minutes after firing has commenced the combination of sulphur and mercury is effected with a violent detonation, whilst a flame is projected from the retort. At the commencement of the second stage, which now follows, the sheet-iron hoods are replaced by hoods of clay, and the fire is gradually raised for  $2\frac{1}{2}$  hours, during which time the excess of sulphur is volatilised. At the commencement of the third stage, condensers are attached to the hoods, which are also made of clay, and the fire is raised until the cinnabar sublimes. That known as lump cinnabar deposits first in the cooler portions of the condensers and afterwards in the hoods, this sublimation lasting about four hours. It is complete when flames of burning sulphur are visible from time to time about the hood and condenser. The latter are now removed, and after the greater portion of the cinnabar has been extracted from them they are broken into pieces and the fragments are carefully cleaned from any cinnabar that may adhere to them. Lump cinnabar and scrapings are thus obtained, the latter being added during the next sublimation. Of the lump cinnabar 70 per cent. is obtained from the hoods, 25 per cent. from the first, and 5 per cent. from the second condenser. The lump cinnabar is ground under water to prevent any loss of dust, and to obtain it in the form of as uniform a powder as possible. The mill consists of a fixed stone and a horizontal stone runner, the latter revolving in a wooden casing at the rate of 40 revolutions per minute. The ground cinnabar, known as vermilion, flows from a spout into a clay vessel placed beneath it. If a lighter shade of cinnabar is required, it must be ground repeatedly, up to five times. At each

fresh grinding the distance between the grindstones is decreased. Three grades of vermilion are made, viz., bright red, dark, and Chinese vermilion. To improve its colour, vermilion is subjected to what is known as refining.—This consists in boiling the vermilion with a solution of potash of  $10^{\circ}$  to  $13^{\circ}$  B. in cast-iron kettles. The charge for each consists of 2 cwt. of vermilion and 48 to 50 lb. of lye. The boiling lasts for ten minutes. At the end of this time the vermilion is allowed to settle, and it is then ladled into tanks. The lye that is left in the kettle is used to treat two charges more. The vermilion is repeatedly washed with hot water in the tanks, and then freed from excess of water by filtering through canvas. It is finally dried in clay pans at a temperature of  $50^{\circ}$  to  $70^{\circ}$  C. The dry vermilion is crushed under wooden hand-rolls, and is then sent into the market packed in sheepskins or in bags. The production of cinnabar in the wet way, as already mentioned, is kept secret.

# BISMUTH

## PHYSICAL PROPERTIES

BISMUTH has a characteristic reddish-white colour and high lustre. It crystallises in the hexagonal system in obtuse rhombohedra with an angle  $87^{\circ} 40'$ , which have the appearance of cubes. Its fracture is coarsely crystalline. Its hardness is low, between 2 and 2.5, and it is so brittle that it can be pounded. Molten bismuth expands on solidifying by 2.35 per cent. According to Roberts, the specific gravity of solid bismuth is 9.82, of fluid bismuth 10.055. The melting point of bismuth is given by Rudberg and Riemsdijk as  $268.3^{\circ} \text{C.}$ ; by Person as  $270.5^{\circ} \text{C.}$  Ledebur found that commercial bismuth melts at  $260^{\circ} \text{C.}$  According to Classen, pure bismuth produced by electrolysis melts at  $264^{\circ} \text{C.}$  At a high temperature molten bismuth volatilises; its boiling point has not been exactly determined, but according to Carnelly it lies between  $1,090^{\circ}$  and  $1,450^{\circ} \text{C.}$  Bismuth has the lowest thermal conductivity of any of the metals; it amounts to 18 compared to that of silver taken as 1,000. Regnault gives the specific heat of bismuth between  $0^{\circ}$  and  $100^{\circ} \text{C.}$  as 0.0308. The linear expansion of bismuth by heat between  $0^{\circ}$  and  $100^{\circ} \text{C.}$  amounts to  $0.001341 = \frac{1}{746}$  of its length at  $0^{\circ} \text{C.}$  according to Calvert and Johnson. The electric conductivity of bismuth is 1.19 at  $13.8^{\circ} \text{C.}$  according to Matthiesen, that of silver at  $0^{\circ}$  being taken as 100. Bismuth is the most strongly diamagnetic of all bodies.

Commercial bismuth is generally rendered impure by an admixture of foreign bodies, chiefly silver, lead, copper, arsenic, iron, nickel, cobalt, and sulphur, at times also thallium and tellurium, which affect the above-named physical characteristics. When impure bismuth is melted and allowed to solidify, numerous globules of pure bismuth, or if lead and silver be present, of bismuth alloyed



with these metals, are formed. Pure bismuth does not show this phenomenon. It depends upon the fact that the alloys of bismuth with bodies other than lead and silver expand on solidification, and therefore expel the bismuth, or the alloys of bismuth with lead and silver, which will still be fluid on account of their low melting point. This phenomenon must be borne in mind in taking samples of bismuth.

#### THE CHEMICAL PROPERTIES OF BISMUTH AND ITS COMPOUNDS THAT ARE OF IMPORTANCE IN ITS EXTRACTION

Bismuth is not affected in the air at the ordinary temperature. Heated in the air, it is covered shortly before melting with a greyish-black coating of bismuthous oxide; if the heating is continued up to redness, a film of bismuthic oxide forms, which is yellow or green in the case of pure bismuth, but has a violet or blue colour if the metal is impure. At bright redness it burns with a bluish flame to bismuthic oxide, which appears in the form of a yellow smoke. Water free from air does not affect bismuth at ordinary temperatures; when containing air it affects it slowly, converting it into a basic carbonate. Water vapour is decomposed by bismuth only at a white heat, and then but slowly. Bismuth combines directly with chlorine, bromine, and iodine. Nitric acid and aqua regia dissolve bismuth readily. Dilute sulphuric acid and cold sulphuric acid do not attack it; it is, however, dissolved by hot concentrated sulphuric acid with the formation of bismuthic sulphate and the evolution of sulphur dioxide. Dilute hydrochloric acid does not attack it; hot concentrated acid dissolves it, but with difficulty. Bismuth is precipitated as metal from solutions of its salts by metals of the alkalies and the alkaline earths, zinc, manganese, iron, nickel, cadmium, copper, tin, and lead.

#### *Oxides of Bismuth*

Bismuth forms four compounds with oxygen, viz., bismuthous oxide ( $\text{Bi}_2\text{O}_2$ ), bismuthic oxide ( $\text{Bi}_2\text{O}_3$ ), bismuth tetroxide ( $\text{Bi}_2\text{O}_4$ ), and bismuthic anhydride ( $\text{Bi}_2\text{O}_5$ ). Bismuthous oxide ( $\text{Bi}_2\text{O}_2$ ) is obtained in the form of a brown precipitate when a mixture of solutions of bismuthic and stannous chlorides is poured into dilute solution of caustic potash. When dried and heated in the air it burns to bismuthic oxide. Bismuthous oxide is produced in the dry way as a greyish-black powder when metallic bismuth is heated in

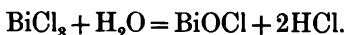
the air to near its melting point. In moist air it becomes more highly oxidised, and when heated in the air is transformed into yellow bismuthic oxide. Bismuthic oxide is obtained by oxidising the metal at a red heat, by heating bismuthic nitrate or carbonate, as also by precipitating bismuthic hydrate from a solution of the nitrate by a solution of potash or soda, and heating the solution to boiling. Bismuthic oxide is a yellow powder soluble in nitric, hydrochloric, and sulphuric acids. It melts at a red heat to a reddish-brown fluid, which solidifies to a yellow crystalline mass. Bismuthic oxide shares this property of fusibility with lead oxide. Bismuth can therefore be cupelled off from silver in the same way as lead. As, however, bismuth is not so readily oxidised as lead, the lead may be partly cupelled off from bismuth; on the other hand, bismuthic oxide is much more readily reduced to metal than lead oxide, so that molten bismuthic oxide is reduced to the metallic state by lead. Bismuthic oxide is reduced to bismuth on a large scale by means of carbon. This oxide shows in its chemical affinities great similarity with the corresponding oxide of antimony. It has but little affinity for acids; its salts are decomposed by the addition of a large volume of water, with the formation of basic salts. Bismuth tetroxide ( $\text{Bi}_2\text{O}_4$ ) corresponds with antimony tetroxide, and may be looked upon as bismuthic bismuthate ( $\text{BiO}(\text{BiO}_3)$ ). It is obtained by melting bismuthic oxide with caustic potash in the air, by igniting bismuthic oxide, caustic potash and chlorate of potash in a silver crucible, as also by treating bismuthic oxide suspended in water with caustic potash and chlorine until the mass assumes a yellowish-red colour. If chlorine is passed for a further period into the solution, compounds of the alkaline bismuthate with bismuthic acid form. By digestion in dilute nitric acid and washing, bismuthic acid ( $\text{HBiO}_3$ ) can be separated. Bismuthic anhydride ( $\text{Bi}_2\text{O}_5$ ) is obtained by heating bismuthic acid to  $130^\circ \text{C}$ . If heated still further, bismuthic anhydride evolves oxygen. It is also decomposed by sulphuric acid and hydrochloric acid, with the evolution of oxygen or chlorine.

### *Chlorides of Bismuth*

Bismuth forms two compounds with chlorine, viz., bismuthous chloride ( $\text{Bi}_2\text{Cl}_4$ ) and bismuthic chloride ( $\text{BiCl}_3$ ). Bismuthous chloride is obtained by heating pulverised bismuth with mercurous chloride, or by melting bismuthic chloride and bismuth together. It forms a black substance which attracts moisture from the air, and is decomposed by water and by dilute mineral acids. When heated

more strongly, it is decomposed into volatile bismuthic chloride and bismuth.

Bismuthic chloride ( $\text{BiCl}_3$ ) is obtained by heating bismuth in chlorine gas, by heating pulverised bismuth with mercuric chloride, and by dissolving bismuthic oxide in hydrochloric acid. It forms a white mass, deliquescent in air, which is volatile at  $427^\circ$  to  $439^\circ \text{C}$ . It is decomposed by water, and if a sufficient quantity of water is employed, the whole of the bismuth present is precipitated as oxychloride in accordance with the equation:—



The oxychloride forms a dazzling white powder, which was formerly used as a cosmetic.

#### *Oxy-Salts of Bismuth*

Of the oxy-salts of bismuth, the sulphate and nitrate are the most important. There are several compounds of bismuth with sulphuric acid which can be produced by dissolving bismuthic oxide in sulphuric acid. From some of these compounds water precipitates basic bismuthic sulphate. Bismuthic sulphate is decomposed on heating, although imperfectly, into the oxide and sulphur trioxide, or sulphur dioxide and oxygen. Bismuthic nitrate,  $\text{Bi}(\text{NO}_3)_3$ , is obtained by dissolving bismuth in nitric acid. It forms colourless crystals with 5 molecules of water of crystallisation. Water precipitates a basic nitrate from the solution, whilst acid salts remained dissolved. Basic bismuth nitrate is used in medicine and as a cosmetic.

#### *Sulphides of Bismuth*

Bismuth forms two compounds with sulphur, viz., bismuthous sulphide ( $\text{Bi}_2\text{S}_2$ ) and bismuthic sulphide ( $\text{Bi}_2\text{S}_3$ ). Bismuthous sulphide ( $\text{Bi}_2\text{S}_2$ ) is obtained in combination with water on treating the solution of a bismuthous salt with sulphuretted hydrogen in the absence of air. A black powder of the composition  $\text{Bi}_2\text{S}_2 + 2\text{H}_2\text{O}$  is thus obtained. In the dry way bismuthous sulphide is produced by melting together sulphur and bismuth in the proportion of their atomic weights. At a strong heat it is decomposed into bismuthous sulphide and metallic bismuth. Bismuthic sulphide ( $\text{Bi}_2\text{S}_3$ ), which is found in nature as bismuth glance, can be obtained in the form of bluish-grey foliated mass by melting bismuth with an excess of sulphur; in the wet way it is produced in the form of a blackish-brown precipitate by passing sulphuretted hydrogen into a solution of bismuthic salts. It is soluble in boiling concentrated hydrochloric

acid and in nitric acid. If water vapour is passed over red-hot bismuthic sulphide, according to Regnault, sulphuretted hydrogen, bismuthic oxide, and a small quantity of metallic bismuth are produced. By passing hydrogen over red-hot bismuthic sulphide, sulphuretted hydrogen and metallic bismuth are obtained. Bismuthic sulphide heated in the air is converted into bismuthic oxide and bismuthic sulphate, sulphur dioxide being evolved. The sulphate is only imperfectly decomposed by increasing the temperature. A mixture of bismuthic oxide and sulphate are therefore always obtained as the products of the oxidising roasting of bismuthic sulphide. Bismuthic sulphide can be melted with metallic bismuth in all proportions. It is said that at very high temperatures the sulphur can be volatilised almost completely. According to Mourlot,<sup>1</sup> bismuth sulphide loses all its sulphur in 10 minutes when a current of 300 ampères at 50 volts is passed through it.

The compounds of bismuth with phosphorus and arsenic are decomposed on heating. Bismuth phosphide is completely decomposed into phosphorus and bismuth. The last portions of arsenic can, however, only be removed with difficulty from arsenide of bismuth.

### *Alloys of Bismuth*

Bismuth alloys with a number of metals, and causes the resulting alloys to melt at a low temperature. Alloys which are used in the arts on account of their low melting points are those of Newton, Rose, Lichtenberg, Wood, and Lipowitz. Their compositions and melting points are shown in the following table:—

Alloy of	Composition.				Melting point.
	Bi	Pb	Sn	Cd	
Newton . . . . .	2	5	3	—	94.5° C.
Rose . . . . .	2	1	1	—	93.75°
Lichtenberg . . . . .	5	3	2	—	91.6°
Wood . . . . .	4	2	1	1	71.0°
Lipowitz . . . . .	15	8	4	3	60.0°

These are used for light solders, for stopping teeth, for taking impressions of woodcuts and coins, and for safety-plugs for boilers.

Zinc will only take up 2.4 per cent. of bismuth, whilst bismuth will take up as much as 14.3 per cent. of zinc. Antimony alloy-

<sup>1</sup> *Compt. rend.*, 1897, 124, I., 768.

with bismuth in all proportions. If an alloy of lead and bismuth is heated in the air to redness, the lead oxidises first, and, after its removal, the bismuth. On account of the easy fusibility of lead oxide, it is therefore possible to separate lead from bismuth by an oxidising fusion of the alloy. When such an alloy is treated by the Pattinson process,<sup>1</sup> the bismuth may be collected in an alloy rich in bismuth, whilst the bulk of the lead is obtained free from bismuth,<sup>2</sup> the bismuth following the silver into the enriched lead. If an alloy of lead and bismuth with silver or gold is heated in the air, the lead is first oxidised, and then the bismuth, the silver or gold retaining a small proportion of the bismuth.

From alloys of gold and bismuth containing but small quantities of gold, the gold may be removed by means of zinc, a small portion of the bismuth being, however, retained in the zinc and gold alloy.<sup>3</sup>

### *Ores of Bismuth*

The ore which furnishes the greatest quantity of bismuth is metallic bismuth. It is found in Europe in the Erzgebirge of Saxony (Schneeberg, Johann-Georgenstadt, Schwarzenberg, Altenberg, Zinnwald); in Bohemia (Joachimsthal), Carinthia (Lölling), Styria (Salzburg), the Banate (Cziklova); Sweden (Fahlun); Norway (Bleka); England (Redruth, Cornwall, and Carrock Fell, Cumberland); Scotland (Alva, Stirlingshire). Outside of Europe it occurs in the United States of North America (Utah), in Peru, Chili (San Antonio del Potrero Grande), and more particularly in Bolivia (Illimani, Tasna, Chorolque, Oruro, Guiana, Potosi, Sorata), and in Australia (Queensland and New South Wales).

Bismuth ochre ( $\text{Bi}_2\text{O}_3$ ), containing 89·7 per cent. of bismuth, and generally intermixed with iron, copper and arsenic, occurs in Bohemia, Siberia, Cornwall (St. Agnes), France (Meymac, Dep. Corrèze), and in Bolivia. This mineral is often mixed with bismuthic carbonate and hydrate. Bismuthic carbonate or hydrocarbonate occurs by itself in Cornwall, France (Meymac), Bolivia, United States of North America (Arizona, Colorado), and Australia (Queensland).

Bismuth glance or bismuthine ( $\text{Bi}_2\text{S}_3$ ), containing 81·25 per cent. of bismuth, occurs in Cumberland, Cornwall, Saxony, Sweden, Bolivia, Colorado and Queensland. The other minerals containing bismuth are of no importance for the extraction of that metal. Among these

<sup>1</sup> Vol. i., p. 625.

<sup>2</sup> Matthey, *Proc. Royal Society*, vol. xiii., p. 89.

<sup>3</sup> Matthey, *loc. cit.*

may be enumerated copper bismuth glance (wittichenite), silver bismuth glance, bismuthic cobaltic pyrites, bismuthic nickel pyrites, bismuthic silicate (eulytine), telluride of bismuth (tetradymitite), tellurate of bismuth, seleno- and sulpho-telluride of bismuth and needle-ore (aikinite).

### *Furnace Products containing Bismuth*

The bismuth which occurs in small quantity in various ores concentrated in certain metallurgical products, the latter of which therefore, form the material for the extraction of bismuth ; among such metallurgical products may be mentioned work-lead, litharge hearths, cupel bottoms, nickel and cobalt speiss.

### EXTRACTION OF BISMUTH

Bismuth is extracted both in the dry way and by means of the wet way. The electrolytic method of bismuth extraction has been proposed for alloys of bismuth and lead, but has not as yet been adopted to any extent. By far the greatest portion of the bismuth that is at present produced is got in the dry way, at the cobalt works at Oberschlema and Pfannenstiel in Saxony, which treat principally ores from Schneeberg and Austro-Hungary, and from the works of Johnson, Matthey and Co., in London, which treat chiefly Australian and South American ores.

The dry method should be used as a rule for ores rich in bismuth and for ores containing bismuth in the metallic state. The wet way is employed for the extraction of bismuth from metallurgical products, from poor oxidised bismuthic ores as also for the extraction or removal of bismuth from the ores which contain it as a subsidiary constituent (tin ores carrying bismuth). Bismuth obtained in the dry or wet way is generally rendered impure by a number of foreign bodies which interfere with its employment for certain purposes, especially for the preparation of pharmaceutical products. It has, therefore, to be refined.

### EXTRACTION OF BISMUTH IN THE DRY WAY

The extraction of bismuth in the dry way from ores varies with the composition of the latter, and depends upon the low melting point of the metal, the decomposability of the sulphide by iron, and the possibility of converting bismuthic sulphide into a mixture of

sulphate and oxide by means of an oxidising roasting, and the reducibility of the oxide by means of carbon, and upon the difficulty of oxidising bismuth in the air at high temperatures. On account of the low melting point of bismuth ( $270^{\circ}\text{C}$ ), it can be separated by simple fusion from the minerals and gangue accompanying it. The fusion may take the form either of a liquation of the bismuth from the accompanying minerals, or of a fusion of the bismuth and accompanying minerals with the formation of a slag. Bismuth is extracted from bismuthic oxide by a reducing fusion with carbon, the other constituents being slagged off. From bismuthic sulphide, bismuth can be obtained either by an oxidising roasting followed by a reducing fusion with carbon, or by melting with iron with the formation of ferrous sulphide and separation of bismuth. From its alloys with lead, bismuth may be extracted by cupellation of the latter until the lead has been removed in the form of litharge. From alloys of the precious metals bismuth may be extracted by cupellation, and reduction of the bismuthic oxide thus obtained by means of carbon. We have accordingly to distinguish :—

- (1) The extraction of bismuth from ores.
- (2) The extraction of bismuth from metallurgical products.

#### i. THE EXTRACTION OF BISMUTH IN THE DRY WAY FROM ORES

Under this heading we have to distinguish :—

- (a) The extraction of bismuth from ores containing it in the native state.
- (b) The extraction of bismuth from bismuthite.
- (c) The extraction of bismuth from ores which contain it in an oxidised state.

##### a. *The Extraction of Bismuth from Ores containing the Native Metal*

Bismuth may be separated from ores containing it in the form of metal, either by a process of liquation or by fusion, in which the entire mass is liquefied. The objection to the process of liquation is that the bismuth is only imperfectly extracted by it, and that other compounds of bismuth, which frequently occur intermixed with the native metal, are not extracted, and remain in the residues. Fusion processes proper, on the other hand, not only yield, on account of the liquefaction of the entire mass, a much better output of native bismuth, but also admit of the addition of desulphurising or

reducing agents to the ores, which will simultaneously extract the bismuth from the sulphur or oxygen compounds that may be contained in the ores, together with the native bismuth. The extraction of bismuth by the fusion process is, therefore, preferable to employing liquation; for which reason the latter process, which was formerly employed, has now been replaced everywhere by the former methods.

### *The Extraction of Bismuth by Liquation*

This process was formerly in use in Saxony. It was carried out in inclined cast-iron pipes, from the lower end of which the bismuth flowed out as soon as it had reached its melting point, whilst the difficultly fusible gangue remained behind. The older liquation furnaces were designed by Plattner, and have been afterwards suitably modified by Günther. Plattner's furnace is shown in Fig. 381, in which *r* is the grate, *E* the furnace body *f, f* are stacks, *s, s* are the inclined cast-iron pipes, which—eleven in number—are arranged in two tiers. (Only half the furnace is shown in the cut.) They are 4 feet long, 10 to 12 inches high and 6 to 8 inches broad, each holding up to 33 lbs. of ore. They are charged from the upper end, which, during the course of the operation, is kept closed by a sheet-iron cover. The liquid bismuth flows out from the pipes through a small opening, *o*, at their lower ends, into two gutters *a*, inclined towards the centre of the furnace, which discharge into a movable kettle, *b*, which is kept heated. Moulds supported upon a carriage are run underneath the lip of the kettle, and the fluid bismuth collected in the latter is poured into them. The residues from the liquation are drawn out at the upper end of the pipes and fall into a box provided with a perforated bottom and standing in water, which can be lifted out from the tank in which it rests. By dropping these residues into water they are at once cooled, and there is nothing to prevent the pipes being immediately re-charged with fresh ore. In a furnace of this kind at Schneeberg, in Saxony,<sup>1</sup> bismuthic cobalt and nickel ores containing up to 12 per cent. of bismuth were liquated. The charge for a tube amounted to 22 to 31 lbs., the liquation of which took from 15 to 20 minutes; the fuel consumption of such a furnace was equal to 590 cubic feet of firewood in 24 hours. The residues still retained one-third of the bismuth present in the ore, and were smelted, forming a bismuthic speiss from which another portion of bismuth was extracted by liquation upon liquation hearths.

The furnace, as modified by Günther, is shown in Fig 382.<sup>2</sup> The

<sup>1</sup> Plattner, *Hüttenkunde*, p. 23.

<sup>2</sup> Kerl, *Metallhüttenkunde*, p. 530.



residues can be more easily removed from this furnace than from the Plattner furnace. The tubes are furnished at their lower end with a

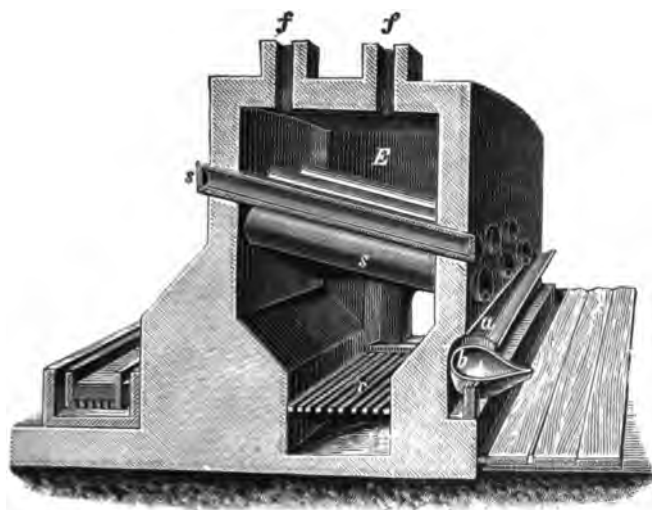


FIG. 381.

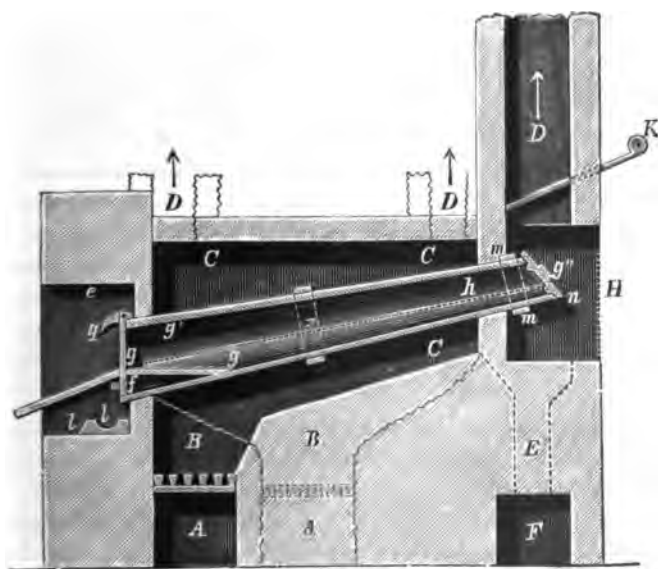


FIG. 382.

rating, *g, g*, made of 7 cast-iron bars, upon which the ore rests. The tubes are charged from their upper end after the cover, *n*, is

removed. The heat generated upon the fire-grate *B* melts the bismuth which flows through the spaces between the bars of the grating, *g, g*, to the opening, *f*, through which it runs out into iron moulds, *l*, standing in front of it. The residues are removed from the lower end of the tubes. For this purpose the cover, which is movable about a hinge, *q*, is lifted up, and the residues are drawn out over the grating on to an iron plate lying in front of the tube.

### *The Extraction of Bismuth by Processes of Fusion*

For the extraction of bismuth by complete fusion, crucible furnaces are best employed. Shaft furnaces have not given satisfactory results because the bismuth rapidly destroys the walls, penetrates into them in consequence of its fluidity, and is slagged off in considerable quantity. As the methods of dry extraction are kept secret, the author does not know whether reverberatory furnaces have ever been used for the extraction of bismuth from ores carrying the native metal. If the native ores contain sulph-arsenides of cobalt and nickel and bismuthic sulphide, the ores are calcined before fusion in order to remove the sulphur and a portion of the arsenic. In order to complete the decomposition of the sulphide of bismuth, iron is added during the process of fusion. Carbon is added for the reduction of the bismuthic oxide, and soda, felspar, lime, quartz or slags may be added to slag off the gangue. At the cobalt works of Oberschlemma, near Schneeberg, ores of bismuth containing cobalt and nickel are first calcined to remove the sulphur and arsenic, and then smelted in the smalt furnaces with carbon, iron and slags, producing, together with metallic bismuth, a speiss containing arsenic, iron, nickel and cobalt, and a slag. The molten mass is poured into iron pans, in which bismuth separates out at the bottom, over it the speiss and the slag on the top. After the speiss and slag have solidified, the bismuth, which remains fluid in consequence of its low melting point, is tapped off from the solidified substances.

At Joachimsthal, in Bohemia, ores containing lead, nickel, cobalt, uranium, silver, iron, arsenic, sulphur and gangue, with an average of 10 per cent. of bismuth, used to be treated by fusion in Hessian crucibles in charges of 1 cwt., mixed with soda (15 to 50 per cent. lime (5 per cent.), fluorspar (5 per cent.), and iron turnings (28 per cent.) under a cover of soda equal to 5 per cent. of the weight of the ore. The fusion was effected in an air furnace, charcoal being used as fuel. The slag that formed was removed from time to time, a corresponding quantity of fresh charge being introduced. The products

were slag, bismuth, and speiss. In 24 hours 2 to 3 cwts. of ore were treated. The crucibles lasted 3 to 4 days. Subsequently the process of fusion was preceded by one of calcination, the ores in quantities of 4 to 10 cwts. being calcined for a period of 4 to 6 hours in reverberatory furnaces fired with lignite. When so much of the slag had been ladled out from the crucible that the entire contents consisted of bismuth and speiss, the latter were poured into conical iron moulds at the bottom of which the bismuth was deposited. After the mass had solidified, the bismuth was knocked off from the speiss and freed from any adhering speiss and other difficultly fusible impurities by liquating in iron tubes. The bismuth contained lead, and was freed from this metal by cupellation. The slag contained uranium, and was treated for the production of compounds of this metal. Since the year 1868, the ores from Joachimstahl have been treated at the smelting works in Saxony.

*b. The Extraction of Bismuth from Bismuth Glance*

Bismuth glance is generally found intermixed with native bismuth. It but rarely occurs in such quantities as to form the material of a separate process for the extraction of bismuth. This is, however, the case with bismuthine occurring in Bolivia. When it occurs intermixed with native bismuth, the ores in question are smelted, either raw or after previous calcination, with a certain quantity of iron, as has been explained under the extraction of bismuth from the ores of Schneeberg and Joachimstahl which contain native bismuth. Ores containing bismuthine alone can either be treated by calcination and fusion with carbon, or in the raw state by fusion with iron. In the one case the chemical processes are the same as in the extraction of lead from galena by the process of calcination and reduction; in the other case the same as in the extraction of lead by the precipitation process. It must be noted that when bismuthic sulphide is calcined, a certain quantity of sulphate is always formed and this salt is only imperfectly decomposed when the temperature is raised, so that there is always a certain quantity of it present in the charge. It is reduced in the fusion to bismuthic sulphide, which passes into the matte, or into the slag if only very small quantities of matte are produced. When ores contain considerable quantities of gangue, the bismuthine may be separated from it by a simple fusion without the addition of iron. Crucible or reverberatory furnaces are used in this process, the fusion taking place in the crucibles in the former case. These are best made 10 to 12 inches

high and 16 inches in diameter at the upper end,<sup>1</sup> the material consisting of clay containing 60 to 70 per cent. of silica and 20 to 26 per cent. of alumina, which is mixed with not more than 20 per cent. of graphite or wood charcoal. Borchers has described a battery of 6 furnaces fired by gas in the work quoted above (p. 58) and also a reverberatory furnace with movable hearth and grate firing (p. 63). As the hearth is quickly corroded by the alkaline charges, it is well to separate it from the fire-bridge and stack by air- and water-chambers. The fire-bridge must be hollow and cooled by air or water. The bismuth and slags are removed from the hearth by separate tap-holes. In Borchers' furnace, the arch and the side walls rest on iron girders so that they are independent of the hearth. A movable hearth is recommended to accelerate repairs, &c., as the alkaline character of the charges shortens the furnace campaigns considerably. Borchers' movable hearth, which can be withdrawn from the furnace on an inclined track, consists of fire-brick resting on stout iron bars. It is advisable to melt down some slag upon the hearth before introducing the charge proper, so as to lessen the loss of bismuth by volatilisation. Valenciennes<sup>2</sup> has made experiments upon the extraction of bismuth from bismuthine from Bolivia, which is at present being treated by some secret process in England. The ores, which occur in Bolivia in considerable quantities, consist of a mixture of sulphides of bismuth, copper, iron, antimony and lead, with small quantities of sulphide of silver. The amount of bismuth in them varies from 15 to 30 per cent. The best process for their treatment has been found to be calcination and reduction. The crushed ores were calcined for 24 hours in a reverberatory furnace with frequent rabbling and intermixture from time to time with crushed coal, and were then smelted in a reverberatory smelting furnace, the calcined ore being mixed with 3 per cent. of coal, lime, soda, and fluorspar. In order to assist the reduction, a reducing flame was kept up for the first two hours, the temperature being a red heat, which was subsequently raised to whiteness. The operation was finished as soon as the contents of the furnace were completely fluid. Together with metallic bismuth, a copper matte containing bismuth and slag were obtained. The molten contents were tapped off at the lowest point of the hearth, and run into conical iron moulds placed in front of the furnace, in which they separated according to their specific gravity, the bottommost layer consisting of metallic bismuth, the next of bismuthic copper matte

<sup>1</sup> Borchers, *The Min. Ind.*, 1900, p. 58.

<sup>2</sup> Note relative à la Métallurgie du Bismuth, *Bull. Soc. Chim.*, 1874.

and the topmost one of slag, consisting chiefly of ferrous silicate. The metallic bismuth still contained lead, antimony, and copper, and had to be purified before it could be used for pharmaceutical purposes. The copper matte obtained, contained 5 to 8 per cent. of bismuth. It was crushed, calcined, and then smelted in the same way as the calcined ore, the products being metallic bismuth and a copper matte which still retained 2 to 3 per cent. of bismuth. Pure bismuth could not be obtained from the latter in the dry way, an alloy of copper and bismuth being always produced, so that the bismuth had to be extracted from this matte by wet methods. Precipitation methods are especially applicable to ores which contain sulphides of arsenic and antimony; these latter metals are thrown out of combination by iron and form a speiss, so that the products of reaction are bismuth, matte, and speiss. Valenciennes employed precipitation processes in reverberatory furnaces experimentally upon these ores, which he had freed from their gangue by a previous fusion. The ores thus prepared, which consisted only of sulphides of bismuth, iron, and copper, were crushed, mixed with 12 per cent. of iron turnings, 30 per cent. of slag, and a certain quantity of soda, and then fused in reverberatory furnaces. After heating for 4 hours up to whiteness, the mass was completely fluid, and was tapped out into conical cast-iron moulds, the products being metallic bismuth, a matte consisting of the sulphides of copper and iron, and slags. The bismuth contained less copper than that obtained by the process of calcination and reduction, but contained antimony. The process worked well, and was much more rapid than the previous one, but had the very great objection that the sulphide of iron rapidly destroyed the hearth of the reverberatory furnace, in consequence of which it was given up.

*c. The Extraction of Bismuth from Ores which contain it in the Form of Oxide*

Oxidised bismuth ores only occur exceptionally in sufficient quantities to be treated by themselves for bismuth. As a rule, they are mixed with native bismuth and are treated together with it. They can be treated by being fused in crucibles or reverberatory furnaces mixed with charcoal. Shaft furnaces cannot be recommended on account of the excessive loss of bismuth, due to slagging and volatilisation. Considerable quantities of hydrated carbonate of bismuth have been found at Meymac, in France. These have, however, been treated by means of the wet

method. If the ores containing native bismuth contain at the same time oxides of bismuth, a corresponding quantity of carbonaceous matter is added during the fusion so as to reduce the oxide of bismuth, the carbon dioxide and water being driven off from the above-named compounds by the action of heat.

## ii. EXTRACTION OF BISMUTH IN THE DRY WAY FROM METALLURGICAL PRODUCTS

Bismuth is at present generally obtained from metallurgical products by means of wet methods. We must distinguish in extraction by the dry way:—

- (a) The extraction from mattes.
- (b) The extraction from alloys.

### *a. The Extraction of Bismuth from Mattes*

Bismuth is extracted from mattes by methods based on the principle of calcination and reduction. The matte is crushed, calcined in reverberatory furnaces until the bismuthic sulphide is converted into oxide and sulphate, and then smelted with the addition of carbon and suitable fluxes in reverberatory or crucible furnaces. Metallic bismuth is obtained, and, when copper is present in the matte, a copper matte containing bismuth, together with ferriferous slag. As it is not possible to completely decompose the sulphate of bismuth produced during calcination by any increase of temperature, a certain quantity of sulphide is always reproduced during the reduction, which passes into the matte. If only small quantities of matte are formed, this, together with any sulphide of bismuth, passes into the slag. A simple precipitation process is not to be recommended for matte, especially when the latter only contains small quantities of bismuth. The method of treating the matte produced in smelting Bolivian ores has already been explained. The details of the process are kept secret.

### *b. The Extraction of Bismuth from Alloys*

Alloys from which bismuth can be obtained in the dry way, and from which it used formerly to be so obtained, are its alloys with lead, and with lead and the precious metals. When a lead-bismuth alloy is submitted to an oxidising fusion, the lead is first oxidised, the bismuth only commencing to oxidise when the greater proportion of the lead has been removed. The cupellation of a lead and bismuth alloy

can therefore be so conducted that the first product is litharge, the next litharge containing bismuth, and the last, if the oxidation is stopped at the right moment, metallic bismuth. Such a cupellation process was formerly employed at Joachimsthal for the extraction of bismuth. The lead bismuth alloy was cupelled in quantities of 4 to 5 cwts., the first product being litharge free from bismuth, which was sent to the lead works, then a brown litharge containing bismuth, and finally a black oxide of bismuth free from lead, on the appearance of which the metallic bismuth, then free from lead, was tapped into cast-iron pans. The litharge containing bismuth was smelted in crucibles together with the cupel bottoms with a flux consisting of quartz, fluorspar, and iron turnings, the product being an alloy of lead and bismuth, which was again submitted to cupellation. The oxide of bismuth free from lead was smelted under a cover of salt with a mixture of quartz, lime, and iron turnings. From work-lead containing bismuth, litharge, rich in bismuth, is obtained in the processes of cupellation in the last stage of litharge production. When this litharge is submitted to a reducing fusion, an alloy of lead and bismuth containing some silver is obtained. By cupelling the latter, litharge still richer in bismuth is obtained, together with litharge free from bismuth, and blicksilver. The former can again be reduced and the alloy of bismuth, silver, and lead thus obtained, can again be cupelled. On reducing this litharge containing bismuth, bismuth containing both lead and silver is obtained. At present, after the argentiferous litharge has been sufficiently enriched in bismuth, it is treated in the wet way.

#### EXTRACTION OF BISMUTH BY THE WET WAY

Bismuth can be obtained by means of wet methods from ores which contain the metal as carbonate or oxide, and especially from metallurgical products in which the bismuth is in the form of an oxide or an alloy. When bismuth is present as oxide it is generally dissolved by hydrochloric acid, more rarely by nitric acid, which is far dearer; when it is present as metal or alloy, by means of aqua regia or of hot concentrated sulphuric acid. Chloride of iron has also been suggested as a solvent.<sup>1</sup>

Bismuth is precipitated from the solutions either directly or as a basic salt. It is generally thrown down as metal by means of iron; it can be precipitated also by lead, zinc, tin, manganese, nickel cadmium, and copper. As a basic salt it can be thrown down by

<sup>1</sup> *The Min. Ind.*, viii., p. 57.

diluting solutions of its chloride with water, when an oxychloride is precipitated. From the oxychloride, bismuth can be reduced either by fusion with lime and charcoal, or by treating the moist salt with iron or zinc. The addition of lime is necessary when the oxychloride is treated in the dry way, in order to combine with the chlorine. The lime may be used either slaked or as caustic lime. Metallic bismuth thrown down in the wet way is melted in graphite or iron crucibles with the addition, in case of need, of alkaline fluxes.

*Extraction of Bismuth in the Wet Way from Ores*

The wet way has been employed for oxidised bismuth ores at Meymac and for calcined tin ores rich in bismuth at Altenberg in Saxony. The ore treated at Meymac<sup>1</sup> is a hydrated carbonate of bismuth in a quartzose gangue containing small quantities of arsenic, antimony, lead, iron and lime. The crushed ore is treated three times over in earthenware vessels with hydrochloric acid at a gentle heat and under constant stirring. The nearly exhausted ore is treated with fresh hydrochloric acid, whilst the almost saturated acid is allowed to act upon fresh ore, saturated solutions being thus obtained, whilst the bulk of the bismuth is removed from the ore. The bismuth is thrown down from the solution in the form of black powder by means of bars of iron. Immediately after its precipitation, it is separated from the solution, washed with water, pressed in canvas bags, and finally melted in graphite crucibles under a layer of charcoal, and cast in iron moulds. At Altenberg, in Saxony,<sup>2</sup> tin ores containing bismuth and bismuth glance are roasted in reverberatories to remove arsenic and sulphur, and the roasted mass is brought, still hot, into a wooden trough, 12 feet long, 2 feet high, and 2 feet wide; and covered 8 to 10 inches high with dilute hydrochloric acid. After 6 hours treatment, the liquid is run into another wooden trough, where the oxychloride is precipitated by the addition of water. The precipitate contains only traces of lead, but is coloured yellow by iron. To remove this it is dissolved again in hydrochloric acid and precipitated with water, and this process is repeated. The precipitate thus obtained is carefully washed with water, dried, and melted down in a graphite crucible with lime, charcoal and slag from a previous operation; metallic bismuth is thus obtained.

Eulert<sup>3</sup> proposes to treat the finely powdered ore with salt solution and nitric and sulphuric acids, and then to precipitate the oxychloride from the solution by dilution.

<sup>1</sup> Carnot, "Découverte d'un Gisement de Bismuth en France," *Bull. Soc. Chim.* 1874.

<sup>2</sup> *The Min. Ind.*, 1896, p. 55.

<sup>3</sup> Ger. Pat., 130963.



*Extraction of Bismuth in the Wet Way from Furnace Products*

The chief metallurgical products from which bismuth is extracted in the wet way are impure oxides of bismuth, litharge containing bismuth, and cupellation residues containing bismuth, such as are obtained during the cupellation of alloys of lead, bismuth and silver. Attempts have also been made to treat alloys of lead, bismuth and silver directly in the wet way. When work-lead containing bismuth is cupelled, litharge free from bismuth is first obtained. When the cupellation is continued, the bismuth is also oxidised and passes into the litharge, the last portions of the litharge being richest in bismuth, whilst a small portion of the latter metal remains in the silver. By smelting the last litharge, which contains both bismuth and silver, in shaft furnaces with charcoal, bismuth can be concentrated in the work-lead thus obtained, and by cupelling the latter, litharge still richer in bismuth is produced. The concentration of bismuth in litharge may be brought about simply in cupelling lead which is not too poor in silver, by not continuing the cupellation until the silver brightens but interrupting the process when the silver contents of the work-lead have been enriched to about 80 per cent.<sup>1</sup> In this case the bismuth is concentrated in the alloy produced, and when the latter is finally cupelled upon a smaller hearth, it passes into the litharge and a portion of it into the test. Both litharge and test are so rich in bismuth that they can be treated directly by wet methods. At Freiberg, in Saxony, argentiferous lead containing minute quantities of bismuth is split up by the Pattinson process into lead rich in silver (containing 2 per cent.) and carrying bismuth, and into lead poor in silver (containing 0.1 per cent.) and free from bismuth, the latter of which is then desilverised by means of zinc. The lead containing bismuth is concentrated in German cupellation furnaces in quantities of 10 to 11 tons at a time until the silver contents reach 80 per cent., and then refined in silver refining furnaces in quantities of 0.9 to 1.2 tons for the production of fine silver, the lead and bismuth being thereby oxidised. The oxides are partly absorbed by the hearth, which is made of marl, and partly flow off as litharge containing bismuth. The litharge and the hearth generally contain from 5 to 20 per cent. of bismuth, and are crushed fine and then treated with hydrochloric acid in stoneware pots 30 inches high and 36 inches in diameter, the charge for a pot amounting to 1 cwt. To this are added 140 to 155 lbs. of hydrochloric acid and 22 lbs. of water

<sup>1</sup> Vol. i., p. 644.

the action of the acid being promoted by gently heating and continual stirring. In 6 hours the bismuthic oxide, together with a small portion of lead oxide, has been dissolved, the residues consisting of chloride of lead and metallic silver. Water is added until the liquid becomes turbid owing to the separation of bismuthic oxychloride. The solution is then allowed to stand for 7 hours in order to clear, and is drawn off by means of leaden syphons into wooden vats 6 feet high and 5 feet in diameter, in which it is diluted with a sufficient quantity of water to throw down the bulk of the bismuth as basic chloride. As soon as the precipitate has settled, the solution is run off first into settling tanks, and then into a sump in which the copper which it contains is thrown down by means of iron. The precipitate of bismuth oxychloride is then washed with water in a wooden vat provided with a linen filter in order to remove a portion of the chloride of lead. It is then dissolved in hydrochloric acid in order to remove a further portion of the chloride of lead. On dilution of the solution with water the bismuth is again thrown down as oxychloride, the latter being again treated with hydrochloric acid in order to remove any portion of chloride of lead that might be left, and from the solution thus obtained the oxychloride of bismuth is again thrown down with water. The salt is then filtered off, washed and dried, and smelted with lime and charcoal or with soda, glass and charcoal in a cast-iron crucible heated in an air furnace, coke being the fuel used. The products are metallic bismuth and slag. The cast-iron crucible is provided with a foot and is 20 inches high in the clear, its greatest diameter being 12 inches. The charge consists of 28 to 44 lbs. of bismuth salt, 16 per cent. of caustic lime, and 6 per cent. of finely ground charcoal. As soon as the contents are in a state of tranquil fusion the slag is ladled off and the bismuth poured into moulds. It is purified by re-melting. It then contains 0.3 to 0.4 per cent. of lead and 0.025 of silver. The residues which remain when the litharge and the various precipitates of bismuthic oxychloride are treated with hydrochloric acid, are washed with water containing hydrochloric acid, dried, and added to charges containing lead and silver, which are being smelted for work-lead.<sup>1</sup> At the St. Andreasberg Works in the Upper Harz, litharge containing bismuth is produced which is sold to Freiberg for treatment in the wet way. At Frankfort-on-the-Maine, in the works of the German Gold and Silver Refinery, bismuth is prepared in the wet way from skimmings containing bismuth, which are obtained in silver refining.

Processes for extracting bismuth from alloys in the wet way have

<sup>1</sup> *Preuss. Zeitschr.*, vol. xviii., p. 193; *Berg. und Hüttenm. Ztg.*, 1876, p. 79.

been proposed by Mrazek and De Luyne, as to the practical execution of which nothing is known. Mrazek<sup>1</sup> proposed sulphuric acid as the solvent for bismuth contained in argentiferous lead and bismuth alloys. These alloys, which are obtained by repeated reduction and cupellation from litharge containing bismuth, and which contain 50 to 60 per cent. of bismuth, are to be treated in the granulated state with hot concentrated sulphuric acid. Bismuth and silver are thereby dissolved, whilst the lead remains as sulphate in the residues; the silver is to be thrown down from the solution by means of sodium chloride, and the bismuth by means of iron. If alloys of lead and bismuth alone are to be operated on, the bismuth can be thrown down directly by means of iron after the treatment with concentrated sulphuric acid. The spongy bismuth obtained by this means is to be pressed, dried, and then melted. The proposed process of De Luyne<sup>2</sup> refers to the extraction of bismuth from alloys containing tin, lead, and bismuth. These are first to be treated with cold hydrochloric acid, so as to remove the greater portion of the tin. The bismuth is then to be brought into solution by treating the residues with aqua regia, and from this solution the bismuth is to be thrown down as oxychloride by dilution with water. This salt is either to be smelted in crucibles for metallic bismuth, in admixture with chalk and charcoal, or it is to be dissolved in hydrochloric acid and the metal thrown down by treating the solution with zinc and the precipitate pressed, dried, and melted. Another proposed process of De Luyne suggests the employment of nitric acid as a solvent, which dissolves bismuth and lead, whilst the tin is converted into an insoluble oxide; from this solution the bismuth is first to be thrown down as metal by means of lead, and then the lead precipitated as carbonate by means of sodium carbonate.

#### EXTRACTION OF BISMUTH FROM LEAD-BISMUTH ALLOYS BY THE ELECTROLYTIC METHOD

Borchers has proposed the extraction of bismuth from lead containing it, by means of the electric current, and has devised apparatus for this process. He fuses alloys containing lead and bismuth, or lead, bismuth, and silver, under molten alkaline chlorides, through which he passes an electric current. The lead is dissolved as chloride and is deposited as metal at the cathode, or at the bottom of the cathode compartment, whilst with a suitable current density, bismuth

<sup>1</sup> *Oesterr. Zeitschr.*, 1874, Nos. 34 and 35.

<sup>2</sup> *Dingler*, vol. clxvii, p. 289.

and silver remain undissolved, and collect at the bottom of the anode compartment. The construction of the apparatus<sup>1</sup> is shown in Figs. 383 to 385, the first showing the plant and the empty apparatus with the cover removed, Fig. 384 being a vertical cross-section, whilst Fig. 385 shows the left-hand half in vertical longitudinal section, and the right-hand half of the apparatus in elevation. The fusion is performed in a vessel of cast-iron, which consists of two horizontal semi-cylinders *a* and *k*, and a hollow iron frame *v* in the shape of a semicircle. The semi-cylinder *a* forms the anode compartment; its left-hand end is steeply inclined. The sides of the anode compartment are provided with a series of step-like projections. The semi-cylinder *k* forms the cathode compartment, the right-hand side of which is also inclined. The hollow iron frame or ring *v* separates the anode from the cathode compartments. Water circulates in it during the electrolysis, and cools its walls to such an extent that they are coated externally with a layer of solidified alkaline chlorides, which serves to insulate it. The anode and cathode compartments are thus insulated from each other by means of this ring. The water enters the ring through the tube *e* and escapes at *x*. Should anything happen to prevent the circulation, an overflow is provided at *s* until it can be put right. The outer circumference of this iron ring is provided with hollow projections which give it the form of an inverted T in cross-section. The hollow space between these two semi-circular projections is filled with an insulating material consisting of clay, free from carbonaceous matter, sand, and marl. These projections also serve to carry the flanges *f, f* of the two semi-cylinders and thus to unite the various portions of the apparatus. The tubes *p* and *r* serve to regulate the level of the molten mass, and to remove the metals after their separation from each other. By means of the pipe *r*, which opens into the bottom portion of the anode compartment, the bismuth is to be removed, whilst the lead is to flow off through the tube *p*, which opens into the lowest portion of the cathode compartment. The flame, which must be free from soot, traverses the flues *h* which surround this vessel and thus heats it.

The process is as follows:—As soon as the water is flowing through the cooling ring *v*, firing is commenced, and sufficient lead is poured in through the pipes *p* and *r* to partly fill the anode and cathode compartments. A mixture of alkaline chlorides in the ratio of their molecular weights  $\text{KCl} + \text{NaCl}$  is then charged. As this mixture melts but slowly it must only be introduced in small quantities at a time. It is better

<sup>1</sup> *Jahrb. der Electrochem.*, 1895, p. 166.

however, to fuse the mixture in a separate pot and to allow the molten mass to run all at once into the decomposing pot. In order

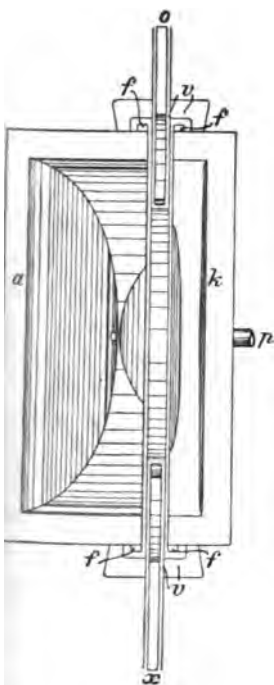


FIG. 383.

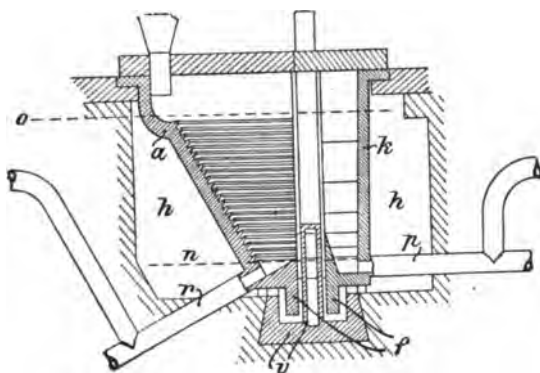


FIG. 384.

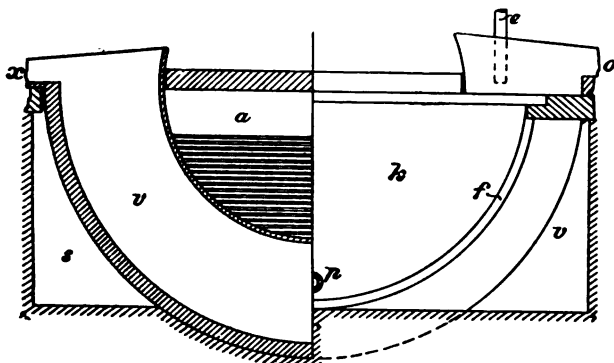


FIG. 385.

to prevent the iron of this vessel, especially at the anodes, from being attacked by the fused mass, it is necessary to make it basic by dissolving in it litharge, or better still lead oxychloride. These lead

compounds must, however, only be added after the pot has been filled with the fused mass, because, otherwise, lead would be deposited upon the metallic portion of the pan, penetrate through the insulation, and thus cause short circuiting. After the pot has been filled with the molten mass, and the external portions of the cooling ring and the iron in its immediate neighbourhood have become covered with a crust of non-conducting and irreducible salts, then the lead compounds have a most beneficial effect upon the electrolysis, and it is preferable to replace the potassium chloride that is volatilised by lead oxychloride. As soon as the first charge of lead compounds has been added, the alloy of lead and bismuth is introduced into the anode compartment by means of a funnel, and a current passed through the molten mass. The molten alloy runs down over the step-like projections of the side of the anode compartment, and the lead in it is dissolved and re-deposited in the cathode compartment, on the bottom of which it collects. On the other hand, bismuth and silver remain undissolved as long as the current tension does not exceed 100 ampères per square foot, and collect at the bottom of the anode compartment. The lead thus obtained is very pure and is tapped off from time to time through the pipe *p*. The crude bismuth contains 90 to 95 per cent. of bismuth and is tapped off from the pipe *r*. The upper apertures of the pipes *p* and *r* must be so arranged that the molten salts reach up to the line *o*, the molten lead up to the line *n*. The bismuth produced contains lead, which can however be readily removed by means of an oxydising fusion. In order to obtain a good separation, it is necessary that the molten alloy should continually present fresh surfaces, so that it is necessary for it to traverse the anode compartment pretty quickly. Complete decomposition is therefore only effected after it has passed through the apparatus several times. Several of these apparatus must therefore be employed, placed stepwise, one below the other, or else the alloy must be caused to pass several times through the same apparatus. With a current density of 100 ampères per square foot the tension required is said to amount to 0.5 volt. Accordingly about 10 lbs. of lead can be separated from the alloy per horse-power per hour. This process has not yet come into use. Borchers states<sup>1</sup> that the results are less satisfactory than those obtained by removing the lead from lead-bearing bismuth by smelting it with bismuth oxychloride.

Electrolytic refining of commercial bismuth has been proposed by Zahorski,<sup>2</sup> the anodes consisting of the impure bismuth cast into plates, the cathodes of carbon, pure bismuth or platinum, and the

<sup>1</sup> *Electro-metallurgie*, 1903, p. 481.

<sup>2</sup> *The Min. Ind.*, 1893, p. 72.

electrolyte of dilute nitric acid. The current density is 15 to 30 ampères per square foot (not exceeding 30). Pure bismuth separates at the cathodes and this is collected, washed with dilute nitric acid dried, and melted down. If the electrolyte becomes too rich in lead (this metal is always present in commercial bismuth), it should be removed from the bath, the bismuth precipitated from solution by lead, and the liquors worked for lead nitrate. Nothing is known as to the application of this process.

According to Borchers (*op. cit.*) there is no difficulty in separating precious metals from bismuth containing them. On electrolysing in weak acid solution these metals remain behind on the anodes, while the bismuth collects in a non-coherent state at the cathodes. Bismuth in this condition is easily fused. Working on a small scale, the electrolysis is carried out in stoneware vessels.

### REFINING OF BISMUTH

Bismuth produced in the dry way contains lead, arsenic, sulphur, iron, nickel, cobalt, antimony, and also silver and gold. The following are analyses of two samples of crude bismuth:—<sup>1</sup>

	Peru.	Australia.
Bismuth . . . . .	93·372	94·103
Antimony . . . . .	4·570	2·621
Arsenic . . . . .	—	0·290
Copper . . . . .	2·058	1·944
Sulphur . . . . .	—	0·430

The amount of gold and silver contained in various qualities of bismuth has been determined by Smith.<sup>2</sup> He found 0·011 per cent. of gold, and 0·3319 per cent. of silver in a sample of Australian bismuth; 0·0003 per cent. of gold and 0·0729 per cent. of silver in a sample of German bismuth; and 0·0005 per cent. of gold, and 0·075 per cent. of silver in a sample of American bismuth. Impure bismuth is not suitable for many purposes for which the metal is employed, and must therefore be purified before use. When it is to be used for pharmaceutical purposes it must be especially pure and, above all things, free from arsenic and tellurium. The purification of bismuth can be performed either in the dry or in the wet way. The dry method produces a metal less pure than the wet way, and in the case of bismuth, which contains a number of foreign bodies, is a very lengthy process, as these cannot be removed by one single operation, but require a whole series. It has the advantage that it is far cheaper

<sup>1</sup> *The Min. Ind.*, 1893, p. 72.

<sup>2</sup> *Journ. Soc. Chem. Ind.*, April 29, 1893, p. 318.

than the wet method, which is also a very roundabout one and only used in special cases.

### *Purification of Bismuth in the Dry Way*

This may consist either in a liquation process or in re-melting bismuth with fluxes of various kinds. Liquation of bismuth is employed in Saxony. It is performed upon a liquation hearth consisting of cast-iron segments forming a groove inclined outwards: the liquated bismuth is cast, just before setting, into iron moulds. Any sulphide of bismuth that may be present then separates out upon the surface of the blocks. The residues that are left upon the liquating hearth, known as *Krätzen*, contain the greater portion of the impurities of the bismuth, and are treated for the extraction of the metals contained in them. If the bismuth is required for pharmaceutical purposes liquation is not always sufficient, and the metal may require further purification by melting or by the wet method.

The purification of bismuth by re-melting in crucibles with various additions is much more perfect than the purification by liquation, but even this is not sufficient in all cases. It must then be repeated until the bismuth is pure. The fluxes that are added depend upon the impurities that have to be removed. If the bismuth contains lead, Borchers recommends fusion of it in cast-iron pots with bismuth oxychloride, salt, potassium chloride, and caustic soda. According to Quesneville arsenic can be removed by melting bismuth with nitre and common salt. This process, the object of which is to form alkaline arsenites, also removes iron and lead. According to Werther, arsenic may be removed by fusing bismuth with one-eighth of its weight of soda and one sixty-fourth of sulphur. In both methods a considerable loss of bismuth is incurred by the formation of bismuthic oxide. According to Thürrach, arsenic, and more particularly the whole of the iron, may be removed by fusing bismuth with chlorate of potash to which from 2 to 5 per cent. of soda has been added. According to Méhu, arsenic may be removed from bismuth by heating the latter considerably above its melting point with excess of air in a vessel presenting a large surface. The greater part of the arsenic is thus removed as arsenic acid, and any sulphur that may be present is converted into sulphur dioxide. The residue has to be remelted with soda, charcoal and tartar or soap, producing an alkaline mass which, when further heated in the air, is freed from the last portions of arsenic and sulphur, which combine



with the alkali. In this process any copper and lead will remain in the bismuth. Johnson, Matthey and Co. heat bismuth<sup>1</sup> containing arsenic in quantities of 10 to 12 tons to a temperature of 395° C. for a considerable time in the air, whereby the whole of the arsenic is volatilised without loss of bismuth. Tamm removes arsenic by dipping thin strips of iron into the bismuth fused beneath a layer of borax at a bright red heat. The arsenic is said then to combine with the iron, and to be completely removed from the bismuth as arsenide of iron. A small portion of iron is, however, retained in the bismuth. Johnson, Matthey and Co.<sup>1</sup> remove antimony by poling the bismuth, which is heated up to the oxidation point of antimony, by means of a piece of wood, the scum produced being removed as long as any forms upon the surface of the bath of metal. For example, 7 cwts. of the molten metal which contained 96·2 per cent. of bismuth 0·8 per cent. of antimony, 0·4 per cent. of iron, 2·1 per cent. of lead 0·5 per cent. of copper, and a trace of arsenic, were heated for 4 hours in the above manner to a temperature of 458° C., at the end of which time the bismuth was free from antimony. The scum contained 30 per cent. of antimony as oxide, and about 10 per cent. of bismuth. Antimony may, moreover, be completely removed by melting bismuth with bismuthic oxide in clay crucibles. The quantity of oxide should be from 2½ to 3 times that of the antimony to be removed. The bismuthic oxide oxidises the antimony to oxide, being itself reduced to metal. The oxide of antimony mixed with a small portion of oxide of bismuth rises to the surface of the bath of metal and is skimmed off it. Borchers<sup>2</sup> removes arsenic and antimony (after lead has been removed by melting with caustic soda, sodium and potassium chlorides, and bismuth oxy-chloride) by melting the metal with caustic soda and nitre, care being taken to avoid overheating; he only melts with soda and sulphur when a considerable proportion of antimony is present. According to Tamm, copper can be removed by melting bismuth with potassium sulpho-cyanate. For this purpose 8 parts of potassium cyanide are mixed with 3 parts of flowers of sulphur and the mixture is thrown on to the molten metal. Potassium sulpho-cyanate is formed with an evolution of heat, so that the compound burns in part, throwing out sparks, the copper separating out in the form of sulphide: any bismuthic sulphide that may be formed is reduced to metal. As soon as the reaction is over and the mass is in a state of tranquil fusion, the slag is allowed to solidify and the still fluid bismuth is poured off.

<sup>1</sup> Matthey, *Chemical News*, 1893, pp. 63-67.

<sup>2</sup> *Electro-metallurgie*, 1895, p. 328; 1903, p. 481.

Together with the copper a portion of the lead, antimony, and arsenic are removed. Copper is also said to be removed by melting the bismuth with bismuthic sulphide, the latter being reduced to metal.<sup>1</sup>

The best method of removing the copper is said to be by stirring sodium sulphide into the molten bismuth, whereby the copper is also separated in the form of sulphide.<sup>2</sup> According to Borchers<sup>3</sup> lead can be removed as soon as the quantity exceeds the fraction of a per cent. by heating the metal with bismuth oxychloride, in quantity corresponding to that of the lead present, in cast-iron kettles under a molten layer of the chlorides of sodium and potassium for a period of 3 hours. As soon as a sample of the metal sets, showing coarse foliation, the refining is finished. After the solidification of the metal the slag is removed by dissolving in water. Borchers considers the removal of lead by melting the metal with caustic soda and nitre, as has often been recommended, to be defective, because plumbates are formed, which being good oxygen carriers, give rise to losses of bismuth. If, on the other hand, the bismuth is free from lead, but still retains arsenic and antimony, these bodies are to be removed by melting the metal with caustic soda and nitre. According to Phillips<sup>4</sup> the Pattinson process is said to separate lead from bismuth with a considerable degree of perfection, the lead passing into the crystals. According to Méhu sulphur can be removed in great part by heating the bismuth above its melting point with excess of air, whereby the former is oxidised to sulphur dioxide. The remainder of the sulphur may be removed by melting the metal containing oxide of bismuth with soda, charcoal and tartar or soap. According to Tamm it may also be removed by melting bismuth with wrought iron. Gold may be extracted from molten bismuth by the aid of zinc. Silver can be removed in the same way. The bismuth may be freed from zinc, according to Mrazek, by the aid of air. If copper, arsenic, antimony, and sulphur are all present in the bismuth, Tamm recommends to remove first the copper, then the antimony, and finally the arsenic and sulphur.

### *Purification of Bismuth in the Wet Way*

This method is dearer than the dry way, but yields on the other hand a purer product. It is only employed when a basic bismuth

<sup>1</sup> *Proc. Royal. Soc.*, vol. xlii., p. 89.

<sup>2</sup> *Tech. Chem. Jahrb.*, 1890-91.

<sup>3</sup> *Op. cit.*, p. 328; 1903, p. 480.

<sup>4</sup> *Elements of Metallurgy*, London, 1891, p. 614.

nitrate is required for medicinal purposes, or when the metal is to be prepared for use in the laboratory. Herapath's process has for its object the preparation of basic bismuth nitrate free from arsenic. He dissolves bismuth in nitric acid, precipitates the basic nitrate by diluting the solution with water, boils the residue with caustic potash or soda to remove arsenic or lead, washes the oxide thus obtained, redissolves in nitric acid, and again precipitates the basic nitrate from the solution by means of water. Deschamps produces pure bismuthic nitrate by dissolving the bismuth in nitric acid, any tin or tin oxide thus remaining in the residue, treating the solution with ammonia, which throws down bismuth whilst copper and silver remain in solution, boiling the precipitate with a solution of caustic potash, whereby lead and arsenic are dissolved, and dissolving the precipitate in nitric acid, and precipitating the basic nitrate by means of water. Schneider dissolves bismuth in nitric acid heated to between  $75^{\circ}$  and  $90^{\circ}$  C., whereby the whole of the arsenic present separates out in the form of arseniate of bismuth with some basic bismuth nitrate. (When cold nitric acid is employed, arsenite of bismuth is formed, which is difficultly soluble in nitric acid, and quite insoluble in bismuth nitrate.) The solution thus obtained is separated from the residues by filtration through an asbestos filter. The clear solution is evaporated, when crystals of nitrate of bismuth perfectly free from arsenic separate out. Hampe has proposed a process for the preparation of pure bismuth for chemical purposes. He melts bismuth with a mixture of sodium carbonate and sulphur, producing bismuth sulphide, which is dissolved in nitric acid after thorough washing; he precipitates the basic nitrate by the addition of water, dissolves it again in nitric acid, and treats the solution with excess of ammonia for the precipitation of bismuthic oxide. The precipitated bismuthic oxide is dried and reduced by hydrogen. The composition of purified commercial bismuth is shown in the following analyses of Schneider :—<sup>1</sup>

	Bolivia.		Saxony.	
	I.	II.	III.	IV.
Bi . . . . .	99.053	99.069	99.390	99.830
Ag . . . . .	0.083	0.621	0.188	0.075
Pb . . . . .	—	—	—	trace
Cu . . . . .	0.258	0.156	0.090	0.040
Fe . . . . .	—	—	—	0.026
Sb . . . . .	0.559	—	—	—
As . . . . .	—	—	0.255	—
Au . . . . .	—	trace	—	—
Tl . . . . .	—	0.140	—	—

<sup>1</sup> *Journ. f. pract. Chem.*, vol. xxiii., p. 75. *Ibid.*, N.F., xlv. 23-48.

## BISMUTH PRODUCED IN 1890 IN THE SMALT WORKS OF SAXONY.

	I.	II.
Bi . . . . .	99·791	99·745
Ag . . . . .	0·070	0·066
Pb . . . . .	0·084	0·108
Cu . . . . .	0·027	0·019
Fe . . . . .	0·017	trace
As . . . . .	—	0·011
S . . . . .	trace	0·042

## SO-CALLED COMMERCIAL "BISMUTH PURISSIMUM."

	I.	II.	III.
Bi . . . . .	99·922	99·849	99·982
Ag . . . . .	—	0·047	—
Pb . . . . .	—	0·049	0·065
Cu . . . . .	0·016	0·019	0·032
Fe . . . . .	trace	trace	trace
As . . . . .	0·025	0·024	trace

# TIN

## PHYSICAL PROPERTIES

TIN has an almost silvery whiteness with a slight bluish tinge and a brilliant lustre. The latter depends to a large extent on the temperature at which it is poured; if the temperature were too high, the surface would show iridescent colours, while if poured at too low a temperature the surface would be dull. The admixture of small quantities of foreign metals (lead, arsenic, antimony, iron, bismuth) also diminishes the lustre of tin.

Tin is dimorphous. It crystallises in the forms of the tetragonal and rhombic systems.<sup>1</sup> The tetragonal form is obtained by reduction from a solution of stannous chloride, or by cooling molten tin at the usual temperature of the air. Rhombic tin is produced by a very gradual cooling of molten tin at a temperature slightly lower than its melting point. The structure of tin is distinctly crystalline; if the surface of tinned plate or tin foil be etched with hydrochloric acid which contains free chlorine, or with stannic chloride, it becomes covered with a pattern resembling frost pictures on windows (*moiré metallique*). A bar of tin emits, when bent, a characteristic creaking noise, the so-called "cry" of tin. This is due to its crystalline structure, the individual crystals grinding against one another on bending.

Many kinds of tin when exposed to severe cold ( $-20^{\circ}$  C.) acquire a rod-like or columnar structure. At lower temperatures still ( $-40^{\circ}$  C.), the rods or columns break up into grey friable grains. These small grains from their characteristic colour are known as the *grey modification* of tin. The exact cause of this molecular change is not known; under these conditions (and presumably as the result of them) certain kinds of tin break up, while others are not affected.

<sup>1</sup> V. Foullon, *Jahrb. der K. K. Geolog. Reichsanstalt*, 1884, p. 367.

If a small quantity of the grey modification be hammered into some ordinary tin, the latter in a short time changes into the grey modification.<sup>1</sup> The specific gravity of cast tin is 7.291, of rolled tin 7.299, of electrically deposited tin from 7.143 to 7.178. That of the grey modification varies about a mean of 7.195 (Rammelsberg), while this variety after re-melting has a specific gravity of 7.310. Commercial tin has a specific gravity of 7.5, most of the impurities in it being heavier than the tin itself.

Tin is harder than lead but softer than gold. It is so extensible at ordinary temperatures that it can be beaten and rolled to thin leaf (sheet tin and tinfoil). At higher temperatures its extensibility diminishes, until at 200° C. it is so brittle that it breaks to pieces when hammered, and can be powdered. If the temperature at which tin is cast be either too high or too low, it will be "short," i.e. brittle. The addition of 1 per cent. to 2 per cent. of copper or lead increases the hardness and tenacity of tin.

Tin is ductile but possesses little tenacity; it is most ductile at about the temperature of 100° C.; a wire 0.08 inch in diameter breaks under a load of 54 lbs.

The melting point of tin is given differently by different observers:—Creighton, 228°, Rudberg, 228.5°, Kupffer, 232°, Person 232.7° C. It boils at a white heat (between 1600° and 1800° C.) and burns with a white flame in the air at this temperature, forming stannic oxide. Its linear expansion by heat, according to Calvert and Johnson, between 0° and 100° C., is 0.002717; its specific heat between 0° and 100° C., according to Regnault, is 0.0562; its conducting power for heat is 145 to 152, when silver is taken as 1000 (Wiedemann and Franz); its conducting power for electricity at 21° C. is 11.45 (Mathiessen) or 14.01 (Becquerel), silver being taken as 100.

Tin is usually contaminated by iron, arsenic, antimony, lead, copper, bismuth, tungsten, molybdenum, and stannous oxide. The effects of these impurities are:—Iron, if present in considerable quantities makes the tin hard and brittle; arsenic, antimony, and bismuth, if present to the extent of 0.5 per cent. reduce its tenacity; copper and lead (1 per cent. to 2 per cent.) make it harder and increase its strength, but make it less malleable; tungsten and molybdenum render it less easily fusible; stannous oxide reduces its tenacity; sulphur is said to render it "short."

<sup>1</sup> *Chem. Zeitung*, 1892, pp. 16, 1197; 1893, pp. 17, 1386.

THE CHEMICAL PROPERTIES OF TIN AND ITS COMPOUNDS, WHICH  
ARE OF IMPORTANCE IN ITS EXTRACTION

Tin at ordinary temperatures is not acted on by either air or water. In air, at temperatures above its melting point, it becomes covered with a greyish-white film, a mixture of stannic oxide and tin, which by continued heating is changed into a whitish-grey powder of stannic oxide, the so-called "putty-powder" of commerce. The complete conversion into stannic oxide is accelerated by raising the tin to a red heat, and also by the presence of lead.

Tin decomposes steam at a red heat, being oxidised to stannic oxide.

Tin dissolves in hydrochloric acid with liberation of hydrogen and formation of a solution of stannous chloride; the concentrated hot acid dissolves it briskly; cold, dilute acid, on the other hand, acts very slowly.

Cold dilute sulphuric acid has very little action on tin; the hot concentrated acid, however, forms with it a solution of stannous sulphate with evolution of dioxide.<sup>1</sup>

Ordinary nitric acid, of specific gravity 1.3, oxidises tin to white hydrated metastannic acid, insoluble in excess of nitric acid; highly diluted nitric acid is reduced by tin with the formation of stannous nitrate and an ammonium salt. The most concentrated nitric acid has no action on tin.

Aqua regia dissolves tin forming stannic chloride; if there be excess of nitric acid present metastannic hydrate is produced.

Warm concentrated solutions of either caustic potash or soda dissolve tin with liberation of hydrogen, forming stannate of potash or soda.

OXYGEN COMPOUNDS OF TIN

We know two compounds of tin with oxygen, stannous oxide,  $\text{SnO}$ , and stannic oxide or stannic acid,  $\text{SnO}_2$ . Stannous oxide acts as a base, while stannic oxide acts both as a base and as an acid.

*Stannous Oxide,  $\text{SnO}$ ,*

is obtained by treating stannous chloride with alkaline carbonates and boiling the resulting white hydrated stannous oxide with water containing a very small quantity of potash, insufficient to dissolve

<sup>1</sup> Recent researches show that stannic, and not stannous, sulphate is formed. See *Journ. Chem. Ind.*, 1898, p. 214.

the hydrated oxide. This oxide takes the form of small glistening black crystals, which are not altered by exposure to air at the ordinary temperature, though when heated in the air they take fire and burn, forming stannic oxide.

The hydrated oxide passes gradually in the presence of water into hydrated stannic oxide.

*Stannic Anhydride,  $\text{SnO}_2$ ,*

is found in nature as *tin stone* or *cassiterite*. It can be produced by heating tin to a high temperature in air, or by igniting stannous hydrate, or stannous oxalate.

Stannic anhydride in the pure state possesses a white or straw-yellow colour which on heating changes to a transient brown. This oxide is reduced to the metal by heating it with carbon, hydrogen or carbon monoxide, and by melting it at a low temperature with potassium cyanide. It is insoluble in all acids, but dissolves in aqueous solutions of the alkalis.

*Stannic Acid,  $\text{H}_2\text{SnO}_3$ ,*

is prepared as a bulky white precipitate by treating stannic chloride solution with ammonia: it is soluble in sulphuric and nitric acids with formation of oxysalts of tin, and in aqueous solutions of the alkalis with formation of salts of stannic acid (stannates).

A modification of stannic acid, the so-called *metastannic acid*,  $\text{H}_{10}\text{Sn}_5\text{O}_{16}$ , is distinguished by its insolubility in acids. It can be obtained as a white powder by treating tin with nitric acid. Ordinary stannic acid is converted by long contact with water into this modification.

## CHLORIDES OF TIN

Tin forms two compounds with chlorine: stannous and stannic chlorides.

*Stannous Chloride,  $\text{SnCl}_2$ ,*

is obtained by acting on tin with hot concentrated hydrochloric acid.

*Stannic Chloride,  $\text{SnCl}_4$ ,*

is prepared by dissolving tin in aqua regia, or by passing chlorine through a solution of stannous chloride, or by burning tin in dry chlorine gas.



## OXYSALTS OF TIN

Among these must be mentioned the *sulphate* and the *nitrate*. The former is prepared by dissolving tin in boiling concentrated sulphuric acid. The nitrate is obtained when tin is treated with dilute nitric acid. The silicates of tin have been but little studied. They are formed by heating stannic oxide with silica,<sup>1</sup> and are readily fusible bodies reducible to tin on heating with iron. Carbon only effects their reduction when some basic substance is present to combine with the silica.

## SULPHIDES OF TIN

Tin forms two compounds with sulphur, stannous sulphide,  $\text{SnS}$ , and stannic sulphide,  $\text{SnS}_2$ .

The *stannous sulphide* is obtained by melting together tin and sulphur, or by the action of sulphur vapour on finely divided tin. It is a leaden-grey foliated mass with a metallic lustre. It can be obtained as a brown precipitate of hydrosulphide by passing sulphuretted hydrogen through a solution of a stannous oxysalt or stannous chloride. Mourlot's investigations<sup>2</sup> show that it is not decomposed on heating electrically, but that it volatilises unchanged.

*Stannic sulphide* can be prepared in the form of golden yellow, glistening scales by heating together tin filings, sulphur, and salammoniac; it is known under the name "mosaic gold." The hydrosulphide can be prepared as a yellow precipitate by passing sulphuretted hydrogen through a solution of a stannic oxysalt or stannic chloride.

*Phosphorus* and *arsenic* combine with tin directly as well as indirectly, forming silver-white brittle substances.

## ALLOYS OF TIN

Tin alloys with most metals in almost any proportion; of these alloys many, on account of their special properties, are applied in the arts. Among them must be mentioned the tin-copper alloys, *e.g.*, bronze, gun-metal, bell-metal; the tin-lead alloys, *e.g.*, pewter, tin-foil, soft solder; the tin-antimony alloys (sometimes with the addition of lead and copper), *e.g.*, bearing-metal, britannia-metal; the tin-bismuth-lead alloys used for type, calico-printing-blocks, and

<sup>1</sup> Recent researches by Mr. H. Dean, under the directions of the Translator, seem to show that stannic oxide and silica do not combine, but that only stannous silicates exist; tin would thus be very analogous to iron in the behaviour of their oxides towards silica.

<sup>2</sup> *Compt. rend.*, 1897, 124, I, 763.

castings; the tin-zinc alloys used for imitation silver leaf; and tin amalgam used for silvering mirrors. The tin-iron alloys are of importance in the extraction of tin. These are known as "hard-heads," and are produced in smelting ferriferous tin ores and tin- and iron-bearing slags. The existence of the compounds  $\text{Fe}_3\text{Sn}$ ,  $\text{Fe}_2\text{Sn}$ ,  $\text{FeSn}$ ,  $\text{FeSn}_2$ ,  $\text{FeSn}_6$ , and  $\text{FeSn}_7$ , has been established. The best known alloy is  $\text{FeSn}_3$ , which was investigated by Nöllner and Plattner in 1860, and later by Oudemans.<sup>1</sup> The latter isolated it in a crystalline condition from Banca tin, and determined its specific gravity to be 7.743. It is formed when tin containing iron is melted and allowed to cool slowly. Lampadius, Berzelius, Berthier, and Stölzel have investigated the alloy  $\text{Fe}_3\text{Sn}$ , Stölzel the alloys  $\text{FeSn}_6$  and  $\text{FeSn}_7$ , Caron and Deville  $\text{FeSn}$ , and Lassaigue  $\text{Fe}_2\text{Sn}$ . According to Stölzel when alloys containing more than two-thirds of their weight of tin are liquated, tin melts away and the alloy  $\text{Fe}_3\text{Sn}$  is left behind.

#### TIN ORES

The only ore of tin which is used for the extraction of the metal is *tin stone* or *cassiterite*,  $\text{SnO}_2$ , containing 78.6 per cent. of metal. It is found in lodes, stockworks, and beds, and also in secondary deposits of water-worn particles, the so-called alluvial deposits. The ores obtained from the former deposits are called *lode-tin*, those from the alluvial deposits, *stream tin*; tin ores are also spoken of as *washed tin*, *tin-sand*, *black tin*, *barilla*.

The lodes are found in the older rocks, in granite, gneiss, mica-schist, greisen and clayslate, the *cassiterite* being usually accompanied by quartz, mica, fluorspar, apatite, felspar, soapstone, tourmaline, chlorite, topaz, axinite, sulphides of various metals, mispickel, specular iron ore, magnetic iron ore, native bismuth, wolfram, and molybdenite.

The alluvial deposits are formed by the weathering of the lodes and surrounding rocks. They are therefore usually found occupying old river beds, and mostly in the neighbourhood of the original lode. The ores from them are invariably purer, because by the action of the atmosphere and running water, a portion of the injurious impurities, *e.g.*, arsenides and sulphides, have been decomposed and carried away.

Tin ore is found in England, Sweden, Russia (Pitkaranta in Finland and Transbaikalia in Siberia), Saxony, Bohemia, Spain (in the province of Galicia), Portugal (Zamora), France (Morbihan,

<sup>1</sup> *Jaarboek van het Mijnwezen in Nederlandsch Oost-Indie*, 1890, I, p. 24.

Vaulois, Cieux, Montebbras), in the United States (California, Dakota, North Carolina, Virginia, Alabama), Alaska, Mexico, Brazil, Peru, Bolivia, Chili, China, Japan, Malacca, Java, Sumatra, Banca, Billiton, Carimon, Burma, Siam, Anam, New South Wales, Queensland, Western Australia, and Tasmania, Africa (Congo, Swaziland).

The most important European localities which at present furnish a supply of tin ore are, in England, Cornwall and Devon, where the deposits have been worked since the time of the Phœnicians. The alluvial deposits are exhausted and at the present time the ore is obtained from lodes and branches from them into the enclosing rock. Altenberg, Geyer, and Zinnwald in Saxony, must be mentioned; in these localities the ore is found in stockworks; also Graupen and Schlaggenwald in Bohemia, where it occurs in similar deposits. The quantity of ore produced in Saxony and Bohemia is small in comparison with that obtained from England, Australia, and the East Indies. In France, tin stone is found in Brittany (at Villeder and Piriac) and in Creuse (at Montebbras), but only in small quantities; also in small quantities in Spain (in Galicia).

Beyond the continent of Europe the most important localities where tin has been discovered are:—in the East Indies (alluvial deposits), Banca, Billiton, Sumatra, the Carimon Islands, the Malay Peninsula (Perak, Selangor, Negri-Sembilan, Pahang); in Australia, both alluvial deposits and lodes are found in New South Wales, and Queensland. The most important Australasian locality is Mount Bischoff in Tasmania, where the ore is found in alluvial beds, in lodes, and in stockworks or pockets. A dyke of eurite and porphyry having broken through the Silurian shales and sandstones, these latter are, at their contact with the dyke, cracked and fissured, and the fissures are filled with tin ore, and arsenical and copper pyrites. These sulphides increase in quantity with depth.

Tin is also found widely disseminated in Bolivia at Chorolque, Oruro, Potosi, and La Paz; Oruro is the most important district.

The greatest amount of stream tin is produced in the above-mentioned localities in the East Indies. The greatest quantity of tin is won in the East Indies, England, Australia, and Bolivia.

Tin stone possessing a fibrous structure is known as *wood tin*. The mineral *tin pyrites* or *bell-metal ore* may also be referred to here, as it contains tin to the extent of 25 to 28 per cent. It consists of an isomorphous mixture of the sulphides of tin, zinc, iron, and copper; the only place where crystals of it have been found is Huel Rock, St. Agnes, Cornwall. On account of its rarity it is not used as a source of tin.

## THE EXTRACTION OF TIN FROM THE ORE

The *dry* method is principally used for the extraction of tin, but wet methods are used in some cases to assist in the separation of certain injurious impurities. Different proposals for the treatment of tin stone by electro-metallurgical methods have been made, but they appear to have no prospect of success. Proposals have also been made for the treatment of tin slags in this way, but it does not appear that there has been any practical application of them so far.

Wet methods as well as electrical methods have been applied to the recovery of tin from refuse, especially from tinned plate cuttings.

The metal obtained from tin stone is nearly always contaminated by foreign elements and therefore needs to be purified from them. This purification, the refining of tin, is done in the dry way; it can however, be done with the assistance of wet methods.

We have therefore to distinguish:—

- I. The extraction of tin in the dry way, subdivided into:—
  - A. The extraction of tin from tin stone and from the intermediate products and dross obtained during the process.
  - B. The refining of tin and working up of refinery dross.
  - C. The extraction of tin from skimmings and other forms of dross.
- II. The extraction of tin in the wet way.
- III. The extraction of tin by electro-metallurgical methods.

## I. THE EXTRACTION OF TIN IN THE DRY WAY

### A. THE EXTRACTION FROM TIN STONE

The extraction of tin from tin stone depends upon the reducibility of tin oxide by carbon and carbonic oxide at a high temperature. The reduction only commences at a white heat. If the tin ore be accompanied by oxides of other heavy metals, especially ferric oxide, as is usually the case with lode ores, these are reduced at the same time and the reduced metals alloy with the tin. Stannic oxide acts as a base to silicic acid, and, therefore, if the latter be present, the tin ore will form with it a slag. The alkalis and the alkaline earths towards which stannic oxide acts as an acid, will, if present, likewise form slag. In consequence of the contamination of tin by the heavy metals and the formation of *sows* and *bears*, on the one hand, and the slagging of the tin oxide by silica and alkalis on the other, it is

absolutely essential that the tin ore be freed as far as possible from impurities before reduction, whether the latter is to be performed in reverberatory or in shaft furnaces. This is done partly by mechanical dressing of the ores, and partly by the use of chemical means, such as roasting or treatment with acids. The preliminary cleaning of tin ores, therefore, forms an important part of the extraction of tin. It is not practicable, however, to free tin ore completely from its impurities, and it is, accordingly, necessary that the impurities remaining in the ore after the preliminary treatment should be carried away in a suitable slag. The slags, which contain chiefly iron as basic constituent, take up not only tin oxide but also grains of tin, which they enclose mechanically owing to their high density. They must be treated specially to extract this metal. The greater the quantity of slag formed in tin-smelting, the less is the direct output of tin. If tin-iron alloys are formed in the treatment of mattes and slags, the tin must be extracted from them also.

Tin has not yet been prepared in the electric furnace, though experiments in this direction are being carried out with promising results by Danneel and Kùgelgen at the Technische Hochschule, Aix la Chapelle.<sup>1</sup>

We have therefore under the extraction of tin from tin stone, to consider :—

1. The purification of tin stone from injurious impurities.
2. The reduction of tin ore.

#### 1. THE PURIFICATION OF TIN STONE FROM INJURIOUS IMPURITIES.

The purification of tin stone from the greater part of its impurities is readily done by taking advantage of its high specific gravity, its stability at a calcining heat and its insolubility in acids.

In consequence of the high specific gravity of tin ore, it is possible to remove earths, quartz, silicates, as well as most of the metallic oxides, by mechanical treatment. The stability of tin stone at a red heat allows the hard siliceous pieces of ore stuff to be calcined previous to dressing until they are brittle, and by the oxidation which takes place during the roasting, sulphur, antimony and arsenic are driven off from their compounds in the ore. The insolubility of tin ore in acids permits the removal of bismuth and copper from the roasted ore by means of acids. In many cases the tin ore contains tungsten compounds, such as wolfram  $(\text{FeMn})\text{WO}_4$ , scheelite  $\text{CaWO}_4$ ,

<sup>1</sup> Borchers, *Electre-metallurgie*, 1903, p. 454.

or tungstite  $\text{WO}_3$ . When such ore is fused with alkaline fluxes, e.g. soda or sodium sulphate, at first tungstate, and afterwards stannate of the alkali are formed. By employing a suitable quantity of fluxes the tungsten can be removed while only a trace of tin is lost as stannate. This method for the removal of tungsten from tin ores was tried, but has been abandoned. The causes of its abandonment are said to be the high cost of the process itself, the restricted market for alkaline tungstates, and the loss of tin by the formation of sodium stannate, and also the disappearance of tungsten from the ore in Cornwall. As tungsten compounds, on account of their high specific gravity, cannot be separated from tin ore by dressing, the separation is effected in many places by hand-picking and careful sorting.

With stream tin a mechanical dressing suffices in most cases to produce a pure tin ore; with lode ores, however, roasting, and in many cases solution processes, must be used to assist the mechanical cleaning. If the lode ore contains much quartz or gangue, calcining to render it brittle, and therefore better fitted for crushing, is found useful before the dressing (*Altenberg tin zwitter*).

By the mechanical dressing to which the ore is subjected, either with or without previous calcination, the gangue, earths, quartz, and oxides of the heavy metals are for the most part removed; while the sulphides, arsenides, and tungsten compounds nearly all remain with the ore.

In order to remove sulphur and arsenic, and also to convert the metals with which they are combined, into oxides, the ore is subjected to an oxidising roasting, which is followed by a washing to remove the metallic oxides formed during the roasting. If the ore contains a great proportion of arsenic, as is the case in Cornwall, it is subjected to second roasting followed by another washing, in order to remove the last portions of that impurity. When copper and bismuth are present, the oxides of these metals, which are formed during the roasting process, are extracted by acids before further washing; dilute sulphuric or hydrochloric acid is used for this purpose.

Tungsten used formerly to be removed after the washing by the fusion of the ore with soda or glauber salt. By a judicious combination of these processes—dressing, roasting, and lixiviation—the tin contents of the ore can be raised from between 1 per cent. and 2 per cent. to between 50 per cent. and 70 per cent.

*The Roasting of Tin Ore.*

The dressed ore, which still contains sulphides and arsenic compounds, principally iron and copper pyrites and mispickel, is subjected to an oxidising roasting in a reverberatory furnace. Sulphur and arsenic are expelled in the form of sulphurous and arsenious anhydrides, and the metals with which they were combined are converted into oxides. The arsenious oxide is collected in long flues and condensing chambers, while the sulphur dioxide is allowed to escape.

The dressed ore usually contains between 25 and 30 per cent. of tin.

If much arsenic be present in an ore, the greater portion of it is not removed in a single roasting; such ores must therefore be roasted more than once.

The chemical changes brought about by the oxidising roasting of a finely divided mass of tin ore, iron pyrites, copper pyrites, mispickel, bismuth, and tungsten compounds—such as frequently forms the material for the extraction of tin—are as follows:—

The iron pyrites is partly converted into ferric oxide and partly into ferric sulphate, sulphur dioxide being at the same time liberated. The ferric sulphate, as the temperature rises, is split up into ferric oxide and sulphur trioxide or sulphur dioxide and oxygen. The sulphur trioxide acts on the sulphides, and also on the arsenides, which are still unchanged, oxidising them.

Copper pyrites is changed into a mixture of copper oxide and copper sulphate.

The tin ore remains unaltered, except a small portion which is changed into stannic sulphate.

Bismuth ores are converted into bismuth oxide.

Leucopyrite loses the greater part of its arsenic as arsenious oxide; a small portion of the arsenious oxide, however, is changed to arsenic oxide and forms arseniate of iron with some of the iron.

Mispickel is converted into a mixture of ferric oxide, ferric sulphate and ferric arseniate, with disengagement of oxides of sulphur and arsenic.

Tungsten compounds are unaltered.

The copper in the ore is, as far as possible, converted into copper sulphate, so that the latter may be extracted from the roasted ore by lixiviation.

As the result of the roasting there is obtained a mixture containing an ore, oxides of iron, copper and bismuth, sulphates of copper, and

iron, a little tin sulphate, ferric arseniate, wolfram compounds, and small quantities of unaltered sulphides and arsenides.

Ferric arseniate is moderately stable at high temperatures; in order to decompose it, it is well to mix powdered coal or organic substances such as sawdust or pine needles with the charge. The iron is thereby converted into ferric oxide, while the arsenic acid is by means of the carbon converted into arsenious oxide and suboxide of arsenic, carbon dioxide being produced.

Reverberatory furnaces for roasting are of two kinds: *a*, those in which the roasting chamber is fixed, and *b*, those in which the whole or part of it is movable.

The latter are used in places where the cost of labour is high, or where the ores contain large quantities of sulphur and arsenic, and where there is a large quantity of ore to be handled. This is, for example, the case in Cornwall, where furnaces of the former kind have been almost entirely replaced by those of the latter. Recently, furnaces with partly movable roasting chambers (the Brunton calciner) have given place to the more effective and capacious Oxland furnace, in which the whole chamber moves.

#### *a. Furnaces with fixed Roasting Chambers.*

These possess either elliptical, rectangular or square beds, with only one working door in the short side opposite the fire. The length of the hearth varies from 7 feet 3 inches to 15 feet; the width (in elliptical beds the width of the widest part) is from 5 to 11 feet; the height of the roof above the bed is from 1 to 2 feet. The charge varies with the size of the furnace from  $\frac{1}{2}$  ton to 1 ton.

The arrangement of the furnace used in Saxony is shown in Figs 386 and 387.

The ore is dried on the roof of the furnace and dropped into the roasting chamber through the opening *a*; *d* is the chimney; *c*, a flue by which the arsenious oxide passes to the condensing chambers and towers. The chimney *d* can be completely shut off from the roasting chamber by the slide *b*; similarly the flue *c* can be shut off from the roasting chamber by a slide or a damper.

In roasting ore containing arsenic in this furnace, the slide must, at the beginning, be closed, and the furnace strongly fired. A great quantity of arsenious oxide is given off by the ore, and this, as the chimney is closed, must pass into the condensing chamber. When the arsenious oxide ceases to be given off, carbon is mixed with the charge to decompose the arseniates which have been formed, and



opening into the flue leading to the condensing chambers is closed, and that leading to the chimney is opened; the products of roasting then pass into the air.

If the ores contain very little or no arsenic, the gases from roasting and from the fire are allowed to pass at once to the chimney. With this kind of ore the furnace is at first gently fired, and the temperature gradually raised as the sulphur is driven out of the charge.

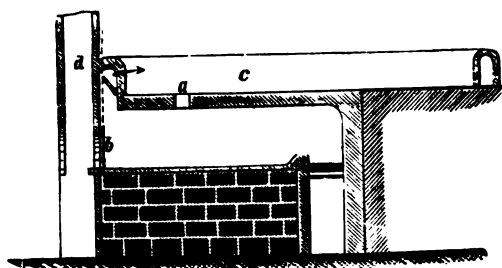


FIG. 386.

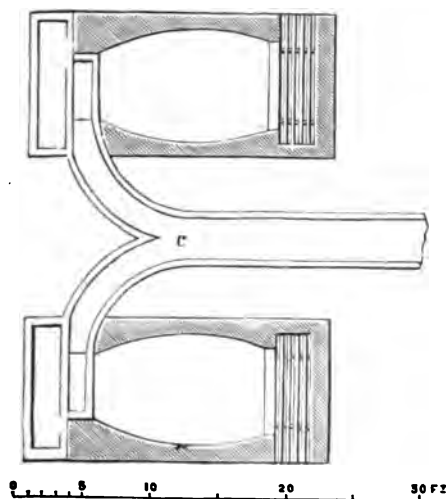


FIG. 387.

During the roasting, the charge must be regularly rabbled and turned from side to side, in order to bring each part of it continually into contact with the air, and also to prevent any fritting together.

A charge contains 12 to 15 cwts.; the time of roasting depends on the amount of arsenic in the ores; those which contain no arsenic will require from 6 to 8 hours, whilst those which do contain arsenic may require as much as 24 hours.

One or two workmen are required for each furnace. At Tostedt (Lüneburg Heath) long-bedded calciners, with two and with four hearths, are used. In the former 2·5 to 4 tons, in the latter 5 to 10 tons of ore, according to the sulphur content of the ore, are worked off in 24 hours.

At Par, in Cornwall, furnaces with elliptical hearths are used: the beds are 7 feet 3 inches long, 5 feet wide, and the height from bed to roof in the middle of the bed is 1 foot  $4\frac{1}{2}$  inches. The flues for condensing the arsenious oxide, more than 300 feet long, are 6 feet 6 inches high and 8 feet 2 inches wide, and have cross-walls projecting alternately from each side; at the end of the flue is a high chimney. The charge consists of 10 to 12 cwt. and remains in the furnace 10 to 13 hours at a gentle red heat, being rabbled at intervals of 20 to 30 minutes. The coal consumption varies from 2 to 2·6 cwt.

Ores containing excessive quantities of arsenic are washed and subjected to a second roasting for 8 or 10 hours.

At Treleighwood, in Cornwall, the furnace bed is 10 feet square, and the fireplace 2 feet 6 inches square. One ton of ore there requires 3 cwt. of coal.

#### *b. Furnaces with partly Movable Roasting Chambers.*

Among furnaces of this kind must be mentioned the Brunton calciner which is used in Cornwall; the construction of it is shown in Figs. 388 and 389, in which *a* is the revolving bed carried by a vertical shaft. It consists of an iron frame, the upper surface of which forms an iron table fitted with concentric ridges; between these ridges are courses of fire-brick. The bed has the shape of a flat cone, the sides of which possess an inclination of  $\frac{3}{4}$  inch to the foot. The diameter varies between 8 and 14 feet. In the furnace figured in the text it is 12 feet.

The vertical shaft, on which a large toothed wheel is keyed, is driven by means of the water-wheel *A* through the cogwheels *k* and bevel gearing *i*. The bed makes  $1\frac{1}{2}$  revolutions in an hour.<sup>1</sup> The roof is 11 inches above the bed; *e* is the hopper through which the ore is fed, and which is fitted with an automatic arrangement for feeding. Above the bed are two or three fixed rakes with inclined tines 3 inches long, fixed in a frame. By the revolution of the table and the inclination of the prongs of the rakes, the ore is gradually worked from the centre to the edge of the table and landed finally at the discharge opening by the movable shoot *g*.

<sup>1</sup> Phillips' *Metallurgy*, p. 513. London, 1891.

Here it is, according to the position of the shoot, which is worked by the handle *l*, discharged alternately into one of the two chambers *h*; the mouth of the chamber, while it is being emptied, is closed with a slide.

In a furnace of this sort 2 to 2½ tons of ore are roasted in 24

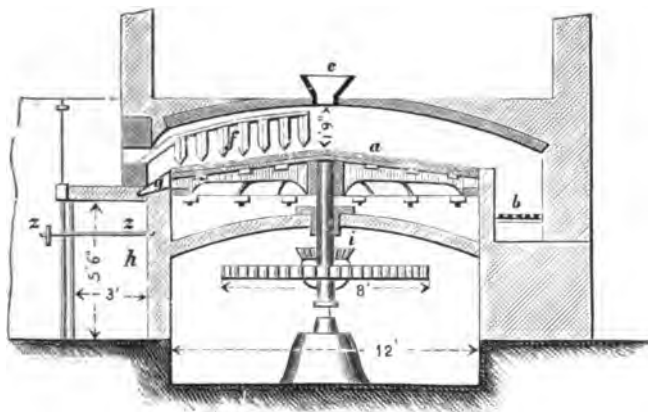


FIG. 388.

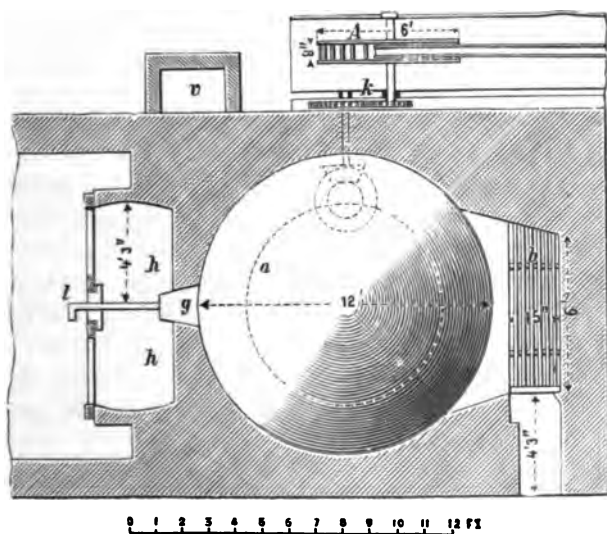


FIG. 389.

hours with a consumption of 2½ cwts. of coal per ton of roasted ore.

The washing of the roasted ore concentrates the tin to about 70 per cent., after which it can be roasted a second time at the rate of

about 3 tons per 24 hours. The Brunton calciner has recently, in many works, been replaced by the revolving calciner of Oxland and Hocking.

*Furnaces with Movable Roasting Chamber.*

Of this kind of furnace that of Oxland and Hocking may be taken as a type. It is used in Cornwall, and has proved itself specially suited for roasting ores rich in sulphur and arsenic.

The arrangement adopted in English tin works is shown in Figs. 390 and 391.

*B* is the revolving cylinder from 30 to 40 feet long, and from 4 to 6 feet in diameter; it is built of boiler plate, lined with fire-brick. As the ore travels forward by the turning of the cylinder, it meets four projecting longitudinal ridges of fire-brick between which it lies. The inclination of the cylinder depends on the nature of the ore to be roasted; with easily roasted ores it is greater than with those that require more time. The cylinder is provided with 3 bearing rings which work on friction rollers *c*. Motion is communicated to the cylinder by the action of the bevel wheel *Z* on the toothed wheel *D*, which is bolted to the shell.

The air which is necessary for oxidation enters the cylinder, warmed by its passage through the flue *i* in the roof *A* of the fireplace. The ore is fed into the upper end of the cylinder through the hopper *h* fitted with an automatic feeder. The longitudinal ridges, by the revolution of the cylinder, alternately raise and drop the ore when it reaches its angle of repose. Thus the ore is brought into repeated contact with the hot gases and air in the cylinder. Having arrived at the lower end of the cylinder, the ore falls through the opening *e* into the arched chamber *F*, from which it is removed through the door *f*. The cylinder makes from 3 to 8 revolutions per minute according to the nature of the ore.

The hot gases and vapours pass from the upper end of the cylinder into the system of condensing chambers *k, l, n, o, p*, in which the arsenious oxide is deposited, and thence to the chimney. The deposit is removed through the openings *m, m*, which are built up during the working. The condensing chambers are covered with cast-iron plates *g*, on which the ore is dried before roasting.

One man and a boy per shift of 8 hours are needed for the working of each furnace. The consumption of coal is considerably

less, and the output considerably greater, than in the Brunton calciner; 20 to 25 tons of ore, according to the amount of sulphur

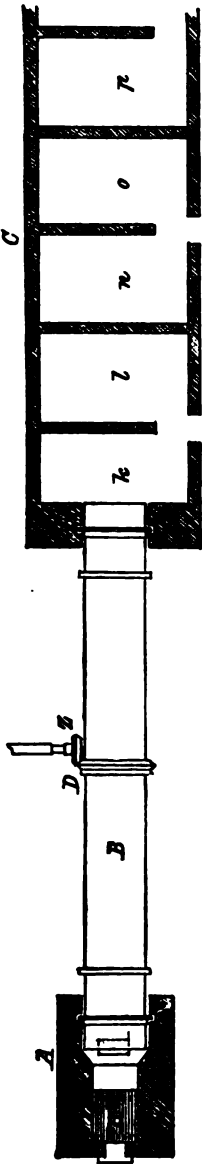


FIG. 390.

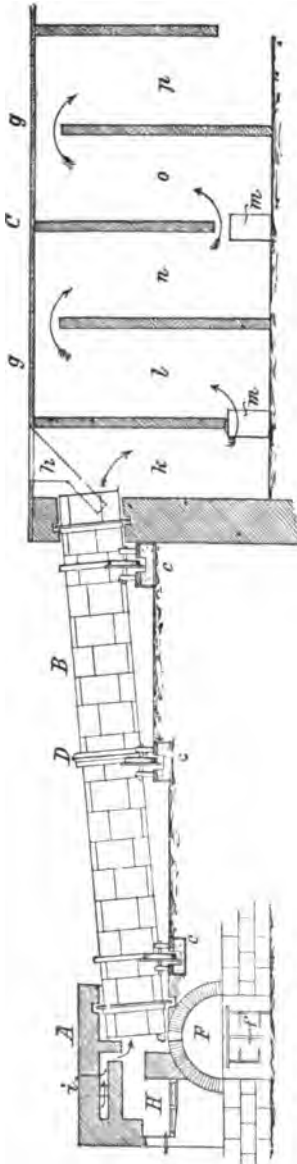


FIG. 391.

and arsenic it contains, can be roasted in 24 hours with the consumption of 1 cwt. of coal per ton of ore.

*Treatment of the Roasted Ore.*

After the ore is roasted for the first time, if it contain copper, it is washed with water, in order to extract the copper sulphate formed during the roasting, after which hydrochloric acid or dilute sulphuric acid is added to dissolve the copper oxide. From the washings the copper is precipitated by scrap iron. Oxides of iron and bismuth will also be dissolved by the hydrochloric acid.

At Altenberg, in Saxony, where the ores contain bismuth, the ore is allowed to remain in contact with hydrochloric acid for many hours in wooden tanks; after this, the solution of bismuth chloride which is obtained is diluted with water in a second set of tanks in order to precipitate basic chloride of bismuth. The liquor is then run off into a row of vats, where the basic chloride settles down, the solution is separated from the precipitate, and the latter dried and smelted in graphite crucibles with lime and charcoal.

*Removal of Tungsten from the Roasted Ore.*

The wolfram, which cannot be removed either by dressing or by extraction with acids or by roasting, used to be extracted at the Drakewells Mine by fusing the roasted and washed ore with soda ash. This process, due to Oxland, depends upon the conversion of wolfram into sodium tungstate which is soluble in water. The process was carried out in a reverberatory furnace, the hearth of which consisted of a shallow cast-iron pan.

The construction of this furnace is shown in Fig. 392; *a* is the cast-iron pan into which the charge is introduced through the



FIG. 392.

opening *z* in the roof; *b* is the fireplace. The flame passes first over the pan and fire-bridge *g*, then down the vertical flue *f* and along under the pan, finally issuing to the chimney *i*, through the

flue *c.* The quantity charged at one time varied from 10 to 11 cwts. ; with coarse ore a greater quantity was charged at one time.

The ore was first charged and the soda ash added as soon as it had attained an incipient red heat. The mass was then well rabbled and brought up to a bright red heat. The quantity of soda ash added was such that a small excess was present beyond that which was needed for the formation of sodium tungstate. In working this process the charge must not be allowed to melt, the particles of tin ore being kept unfused. The charge remains  $2\frac{1}{2}$  to 3 hours in the furnace, after which a portion only of it is drawn off through an opening in the bed (not shown in the figure), into an arched chamber underneath. In 24 hours, 3 to 4 tons of ore can be worked with a consumption of 6 cwts. of coal. The fused mass is placed, while still hot, in lixiviating tanks and there treated with water ; the solution obtained is evaporated either to the strength at which it will crystallise, or to dryness ; in the latter case the residue will contain 70 per cent. of sodium tungstate.

The residue from the lixiviation is washed till the oxides of iron and manganese, formed by the decomposition of the wolfram, are completely removed.

This method has been given up, or is only rarely used ; it is expensive, and there is some loss of tin, consequent on the formation of stannates ; and further, the market for tungsten compounds is limited, and their price is low.

Glauber salt, or sulphate of soda, being cheaper than soda ash, is used in place of it, coal being added to decompose the sulphuric acid. The furnace is first worked with a reducing flame, which with the coal present in the charge reduces the sulphuric acid of the glauber salt to sulphurous acid which escapes ; the furnace is then worked with an oxidising flame by which the wolfram is converted into sodium tungstate and oxides of iron and manganese.

The charge is 9 cwts., and 4 charges are worked in 24 hours. The mass is lixiviated, while still hot, in tanks filled with water. Both solution and residue are treated in the same way as in the soda ash method. This process, which demands great care, has, on the above-mentioned grounds, also been given up.

A method has been proposed by Michell for treating ores which contain at the same time copper and wolfram. The ore is subjected to a chloridising roasting with common salt, by which the wolfram is converted into sodium tungstate, and the copper to copper chloride ; arsenic, antimony, and bismuth, if present, will be volatilised as chlorides. From the solution which will contain the copper and

tungsten, the former can be precipitated with iron, and the latter by calcium chloride as calcium tungstate. This practice has also been given up, though it was for a time used in Bohemia and Cornwall.

At present the most practical way is to separate the wolfram from tin ores by hand-picking.

Ore which has been once roasted and washed, if it is free from sulphides and arsenides, or if it contain very small quantities of these, is smelted for the production of tin. If, however, it contains considerable quantities of these impurities, as is usually the case in Cornwall, it is subjected to another roasting and washing for the removal of the last portions of the sulphur and arsenic, and of the oxide of iron formed in the roasting. This second roasting and washing would be performed in the same plant as the former ones, and the ore, after this treatment, would be smelted to produce tin.

In Bohemia, Saxony, and some English works, ores are only once washed and dressed. The dressing of the roasted ores is done by washing.

## 2. THE REDUCTION OF TIN ORE.

The reduction of tin ore is effected by smelting it with carbon.

The reduction process can be carried out in a shaft furnace or in a reverberatory furnace. At present about two-thirds of the world's tin is produced in shaft furnaces of small dimensions from comparatively pure ores, wood charcoal being used as fuel and reducing agent. There are no practical results to hand of the use of large furnaces worked with coke, as in the smelting of copper and lead ores. Thus one can only say that small furnaces, worked under the conditions just mentioned, are effective, considering the small output of tin required. It may be added that in general they produce slags poorer in tin than reverberatory furnaces; that the tin is less pure owing to the strong reduction that takes place; that more tin is volatilised; that pulverulent ores require the addition of loosening agents (slags being used for this purpose), and as a result the quantity of slag is increased and tin lost thereby; and that when coke is used, the large amount of ash it contains, which must be slagged off, leads to the formation of much slag, and the increased blast pressure required causes greater loss of tin by volatilisation. Finally, the recovery of tin from slags and alloys requires repeated smeltings, which are better performed in reverberatories than in shaft furnaces.

The reverberatory furnace needs no addition of any material to



charges of fine ore for the purpose of loosening it; but only of coal (usually lean coal) for reduction purposes. As fuel for heating is not in contact with the charge of ore, the slagging off of a considerable quantity of ash is obviated. It requires no blast, and it allows of the use of solid crude fuel, as well as of gaseous and liquid fuels; it is capable of a greater output than the shaft furnace, and permits of the production of a purer tin. On the other hand, the siliceous hearth increases the slag, and the slags are richer in tin than those from the shaft furnaces; the linings, too, require larger quantities of fire-brick in the former case than in the latter. The slags and bye-products are, however, capable of simple treatment in the reverberatory furnace. These furnaces are used at present for rich and poor ores, for fine ore and lump ore, and in places where fuel and fire-proof materials are cheap and where large quantities of ores have to be worked up. It is at present impossible to say with certainty whether large shaft furnaces with flue dust chambers would be preferable or not to reverberatories. Apart from the early methods for the treatment of tin stone in hearths built in the ground, shaft furnaces were in general use up to the year 1705, when reverberatory furnaces were introduced into Cornwall.<sup>1</sup>

#### *a. The Reduction of Tin Ore in Shaft Furnaces.*

The extraction of tin in these furnaces is practised in Saxony, Bohemia, Finland, Bolivia, Billiton, Banca, and the Malay Peninsula, in Siam, Burma, South China, and Japan.

Shaft furnaces must be low because, otherwise, foreign oxides would be reduced and their metals would alloy with the tin; *sows* would also be formed in the furnace. They are, therefore, not built more than 10 feet in height. The furnaces used so far have had but little depth and width; in recent times, however, American furnaces with water jackets have been tried. The working results of these are unknown.

In order that the tin may get away as quickly as possible from the oxidising action of the blast, and to prevent the formation of *sows* on the sole-block, these furnaces are always built on the "*Spur*" principle,<sup>2</sup> and are usually worked with an open taphole or *eye*. They are provided with dust chambers to collect the volatilised tin and the fine ore which is carried away by the blast.

The construction of a furnace at Altenberg, in Saxony, is shown in Figs. 393 and 394.

<sup>1</sup> Pryce, *Mineralogia Cornubiensis*, 1778, p. 282.

<sup>2</sup> i.e. with an arrangement by which the tin collects in a fore-hearth (*Vortiegel*) outside the chamber in which the reduction takes place. See vol. i. p. 118.

In these *k* is the inner lining of granite 10 feet 2 inches high, which is enclosed on three sides by the granite or gneiss outer wall *r*; *v* is the front wall. The sole-block *o* is formed by a granite slab inclined at an angle of  $26^{\circ}$ , and often covered over with a brasque of

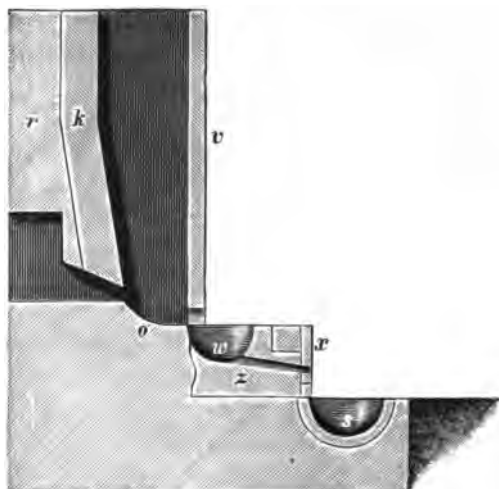


FIG. 303.

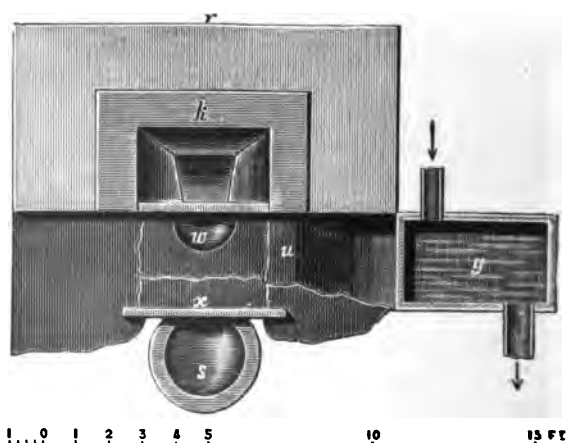


FIG. 304.

fire-clay containing a certain proportion of coal dust. The furnace cavity which diminishes in area from above downwards is trapezoidal in horizontal section. The blast enters through two tuyeres in the back wall of the furnace.

The fused products pass through the open *eye* of the furnace into the fore-hearth *w*, hollowed out of a slab of brasque which forms the fore-hearth of the furnace. Here the tin and slag separate from each other; the slag is allowed to flow over the slag-notch and over an iron plate *u* connected with it; into the tank *g*. The latter is filled with water, and by means of supply and discharge pipes can be kept at a fixed temperature. The slag, which contains tin mechanically enclosed, is chilled in the water and is thereby brought into a suitable state for subsequent crushing. The tin is tapped through the taphole *z* from the fore-hearth into the tapping pot (*Stechherd*) *s*;

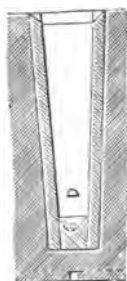
Section on *a b*Section on *c d*

FIG. 396.

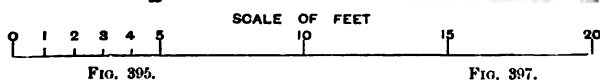
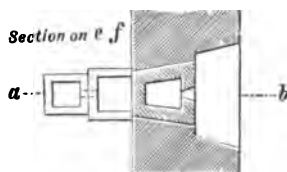
Section on *e f*

FIG. 396.

FIG. 397.

The taphole is  $3\frac{1}{2}$  inches wide, and passes through the iron plate *x*, which is  $4\frac{1}{2}$  inches thick. The pot is made of either cast-iron or granite, with a lining of clay, and is 1 foot 7 inches in diameter and 1 foot 4 inches deep. Beyond the furnace is a system of dust chambers not shown in the figure.

The construction of a furnace at Graupen, in Bohemia, is shown in Figs. 395–397.

One tuyere only is used, and the shaft is 8 feet  $10\frac{1}{2}$  inches high and trapezoidal in horizontal section. The sectional area of the shaft is diminished from above downwards by the convergence of

the side walls. The lengths of the parallel walls at the mouth are :—the front 1 foot 6 inches and the back 1 foot 8 inches : at the tuyere level the lengths are :—the front 10 inches, the back 10½ inches. The inclined sole-block is formed of a fine-grained sandstone ; formerly porphyry was used for this purpose. The inner lining is built of fire-brick.

The shaft furnaces which were in use before 1705 in Cornwall were arranged as *Sumpfföfen*<sup>1</sup> (See vol. i. p. 118).

At Pitkaranta in Finland cylindrical shaft furnaces 10 feet high and 1 foot 6 inches in diameter were in use. In China, a water-jacketed furnace of American pattern with Root's blowers is said to have been introduced, though nothing is known as to its working.<sup>2</sup> At Potosi in Bolivia, also, a similar furnace has been introduced with favourable results, though no details are forthcoming.<sup>3</sup>

The older forms of Chinese furnaces, both draught and blast, are extensively used in the Malay Peninsula. The arrangement of a

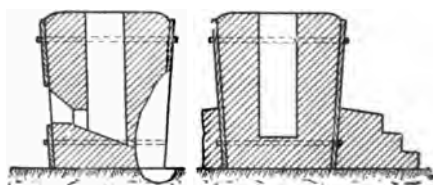


FIG. 398.

FIG. 399.

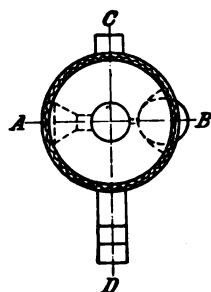


FIG. 400.



FIG. 401.

draught furnace as seen by Louis<sup>4</sup> in the Tras District is shown in Figs. 398–401. It is made of wooden stakes and clay, the stakes being held together by bands of rattan. The air is let in through two fire-clay pipes, 3 inches in diameter, which are placed in the back wall of

<sup>1</sup> Pryce, *op. cit.*, 272.

<sup>2</sup> *The Min. Ind.*, 1896, p. 562.

<sup>3</sup> *The Min. Ind.*, 1896, p. 561.

<sup>4</sup> *Ibid.*, 1896, p. 544.

the furnace. The draught is regulated by plugging these pipes. Compact wood charcoal and pure lump ore are needed for these furnaces. They have been replaced in greater part by blast furnaces. These are constructed as follows:—wooden stakes 8 feet long were fixed in the ground close together, so as to form an inverted truncated cone 6 feet 6 inches high, with a diameter at the top of 5 feet, and at the bottom of 3 feet 4 inches. They were then bound together with flat bands of rattan, and the whole of the interior of the cone filled with clay well rammed together; in this the furnace cavity proper was then hollowed out. This cavity was 5 feet deep and had a diameter at the top of 1 foot 6 inches, and at the bottom of 10 inches. The opening by which the blast was admitted was placed  $3\frac{1}{2}$  inches above the lowest point of the cavity. The primitive blower was made out of a hollowed tree trunk, with two air exits and slack valves, and a piston which was moved backwards and forwards<sup>1</sup> by a coolie.

The construction of an old Chinese furnace at Dreda is shown in Figs. 402–404.<sup>2</sup> It is a *Tiegelofen*, the taphole of which is closed

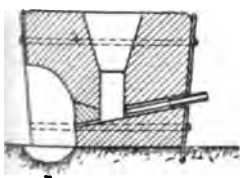


FIG. 402.

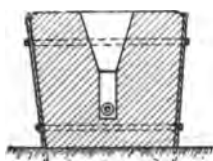


FIG. 403.

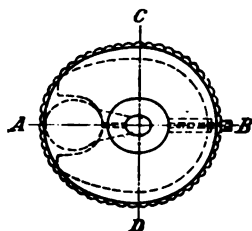


FIG. 404.

during working by a clay plug. The blast is conveyed through a clay pipe in the back wall of the furnace.

The shaft furnaces in the larger works in the State of Perak in the Malay Peninsula are built of brick with an outer wall of rough masonry, and are worked with a fore-hearth with open *eye*. They are 6 feet 6 inches high from the level of the floor. The cavity is semi-circular in cross-section and has a diameter at the top of 1 foot 6 inches, which diminishes to 6 inches at the *eye*.

The construction of a furnace of this kind can be seen from Figs. 405 and 406. It has only one opening for the admission of the blast, which is produced in the primitive manner described above in connection with the older form of Chinese furnace. A is the outer

<sup>1</sup> Cramer, *Oesterr. Zeitschr.* 1894, p. 543.

<sup>2</sup> *The Min. Ind.*, p. 548.

casing, *B* the cavity, *C* the *eye*, *D* the fore-hearth, *F* the tuyere inclined at an angle of  $40^{\circ}$  or  $45^{\circ}$ , *G* the blower, *E E* are stages leading

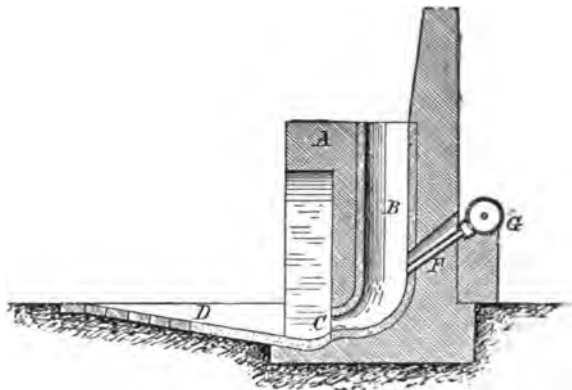


FIG. 405.

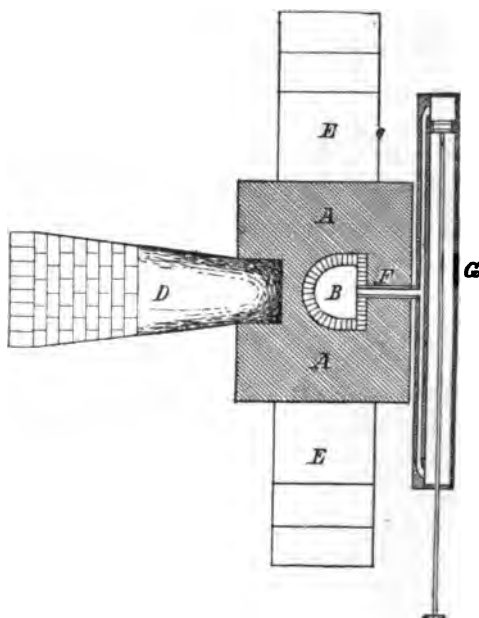
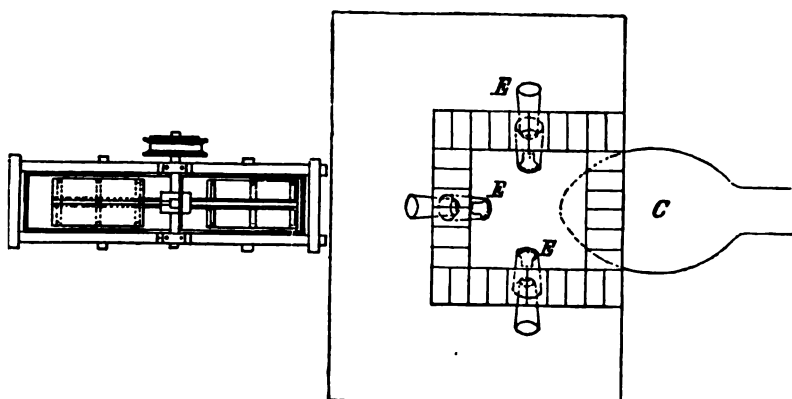
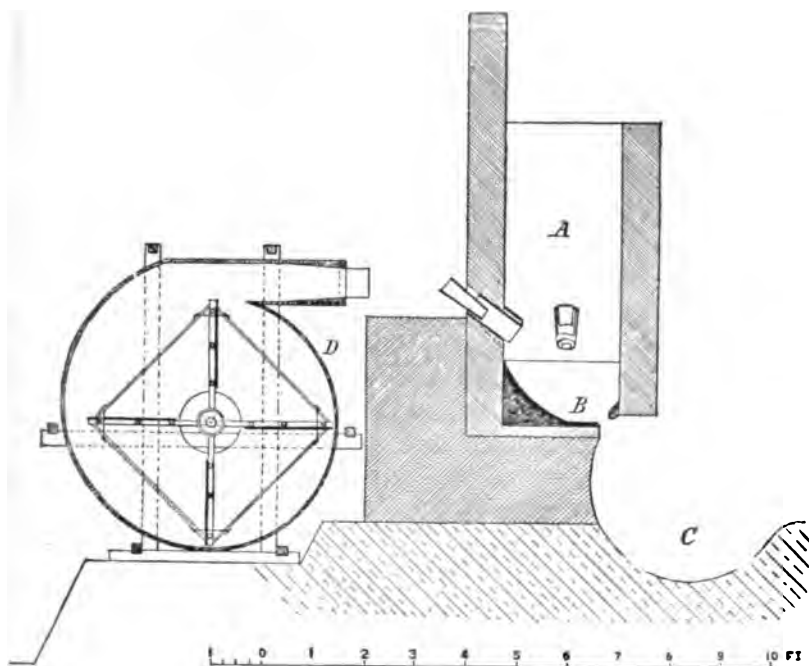


FIG. 406.

up to the mouth of the furnace. The blower requires the services of 3 coolies.

In Banca and Billiton Chinese furnaces were supplanted in 1868 by Vlaenderen's furnaces. In the year 1875, 90 of these furnaces were in use in Banca alone, and at present they are exclusively in

operation in Banca and Billiton. They are three-tuyered furnaces worked with a fore-hearth, and are square in section internally.



FIGS. 407 and 408.

They are 9 feet 2 inches in height, and the blast is supplied by a fan ; the construction of one is shown in Figs. 407 and 408.<sup>1</sup>

<sup>1</sup> *Jaarboek v. h. Mijnwesen in Nederlandsch Oost-Indie*, 1872.

*A* is the shaft, *B* the open eye (taphole) of the furnace, *C* is the fore-hearth (cavity in which the runnings collect), *E, E* are the tuyeres, *D* is the fan. These furnaces have replaced the older Chinese furnace with advantage. The smelted tin is ladled out of the fore-hearth into iron moulds and sent to market, the hard tin (*hardhead*) ( $\text{FeSn}_2$ ) which remains behind (in the fore-hearth) being first liquated.

The ore in Saxony and Bohemia is mixed with slags from a similar previous process and dross, the slag which is added serving as a loosening material and as a flux. In the Malay Archipelago and Peninsula, where pure ores are treated, no slag is added. The tin oxide is reduced to tin by the carbon of the coal and the carbonic oxide formed in the process. Louis<sup>1</sup> is of the opinion that potassium cyanide, produced by the action of nitrogen upon the potash in the charcoal ash, plays an appreciable part in the reduction process. The foreign constituents of the ore pass chiefly into the slag, but part of the metals reduced from them, especially iron and copper, alloy with the tin. If the ores contain wolfram, part of the tungsten is found in the slag, and part in the tin. In this case the slag will be less fusible.

Tin and slag together run from the furnace into the fore-hearth and arrange themselves according to their densities; if the tin contain iron, a difficultly fusible alloy of tin and iron, the so-called *hardhead*, frequently separates out in the fore-hearth. The slag is either lifted off the tin or allowed to run over the slag-notch (generally into a tank containing water). The tin is usually tapped from the fore-hearth into a tapping pot placed in front of it.

The amount of slag added to the ore (in European practice) may be as much as 50 per cent.; the total quantity worked depends on the size of the furnace, and amounts to upwards of 3 tons in 12 hours. The products are crude tin, slag, and hardhead.

The crude tin from the blast furnace is still impure and must be refined. Its composition, according to an analysis by von Lill of a sample from the Schlaggenwald in Bohemia, is:—

Sn . . . . .	97·339 per cent.
Fe . . . . .	0·684   "   "
Cu . . . . .	2·726   "   "
As . . . . .	trace
S . . . . .	trace

---

100·749

<sup>1</sup> *The Min. Ind.*, 1896, p. 536.



Tin produced in the Malay Archipelago in the old Chinese furnaces is of great purity, as shown by the analysis:—

Tin from Siak <sup>1</sup>	Tin from Banca <sup>2</sup>
Sn . . . . 99.96	99.90
Fe . . . . 0.03	0.20
S . . . . trace	trace

The slags are silicates of the metallic oxides contained in the ores, particularly ferrous, manganous, and aluminous oxides with small quantities of silicates of lime and magnesia. They also contain tin oxide, partly combined with bases, partly with silica, and partly as undecomposed oxide mechanically held by the slag. When wolfram is present in the ore, the slags will contain also tungstates of iron and manganese. They are, according to the proportion of silica which they contain, a complicated mixture of mono- and bi-silicates with variable quantities of compounds of stannic and tungstic acids; and they always contain considerable amounts of metallic tin partly in a state of fine division and partly in the state of coarse prill.

As long as the slags contain a fair amount of silicate of tin, no iron is separated in the metallic condition, since iron decomposes silicate of tin, forming tin and iron silicate.

The composition of these slags can be seen from the two following analyses of specimens from Altenberg:—

	I. Lampadius. Per cent.	II. Berthier. Per cent.
SiO <sub>2</sub> . . . . .	20.05	16.0
SnO <sub>2</sub> . . . . .	25.12	32.0
WO <sub>3</sub> . . . . .	—	1.0
FeO . . . . .	30.15	41.0
MnO . . . . .	—	1.7
CaO . . . . .	1.10	3.7
MgO . . . . .	1.23	1.7
Al <sub>2</sub> O <sub>3</sub> . . . . .	5.0	2.4
	<hr/> 82.65	<hr/> 99.5

The slag, after crushing and washing to free it from prill, is subjected to repeated smeltings with charcoal in shaft furnaces in order to extract the tin it contains. The first time this is done

<sup>1</sup> *The Min. Ind.*, 1896, p. 559.

<sup>2</sup> *Berg.- und Hütt. Jahrbuch*. 1864,

(the so-called *Schlackenverändern*), it produces slag-tin (*Schlackenzinn*) and a slag which contains mechanically a large quantity of metallic tin. This slag is smelted again and yields *Schlackenzinn*, and a second slag which still retains metal mechanically. These latter slags, as well as slags rich in tin from the preceding processes, are subjected to a process of dressing, in order to get a product rich in tin, which can be added to slag- or ore-charges; at the same time, the refuses obtained in smelting and refining, such as liquation dross, hardhead, skimmings, furnace dross, and flue dust, are worked up.

The smelting of slags is done either in ore furnaces, following immediately upon the ore smelting, or in special shaft furnaces of small height to prevent the reduction of ferrous oxide.

It frequently happens in smelting ores containing iron, and more so in smelting slags, that tin-iron alloys (hardhead) are formed, which deposit in the fore-hearth. These alloys, which have a grey or white colour and a crystalline structure, and are very brittle, are formed in consequence of the property of tin of uniting in all proportions with iron to form a series of homogeneous alloys. Alloys of this kind possessing the formula  $\text{Fe}_4\text{Sn}$  (Berthier),  $\text{Fe}_2\text{Sn}$  (Deville and Caron),  $\text{FeSn}_2$  (Nöllner) and  $\text{FeSn}_6$  and  $\text{FeSn}_7$  have been isolated.

The composition of hardhead from Altenberg in Saxony will be seen from the following analyses.—

	$\text{Fe}_4\text{Sn}$ .			$\text{FeSn}_2$ .
	I. Lampadius. Per cent.	II. Berzelius. Per cent.	III. Berthier. Per cent.	IV. Plattner. Per cent.
Sn . . . . .	30.5	31.4	32.22	80.89
Fe . . . . .	61.5	62.6	64.14	17.16
W . . . . .	0.9	1.6	1.64	—
As . . . . .	1.45	—	—	—
Cu . . . . .	—	—	—	0.99
Carbon . . . . .	0.95	—	—	0.96
Slag . . . . .	3.51	2.4	—	—
	98.81	98.0	98.00	100.00

Hardhead is smelted with the other refuse products of the extraction.

#### *Examples of Shaft Furnace Practice.*

The tin-bearing rock mined in Altenberg and Zinnwald in Saxony, called *Zinnzwitter*, is concentrated by dressing and roasting from  $\frac{1}{2}$  per cent. up to 50 or 60 per cent. of tin, and is smelted with wood charcoal in the above described furnace with the addition

from 25 to 50 per cent. of slag from a previous similar process, 6 or 7 per cent. of dressed furnace dross and variable quantities of washed drosses and hardhead.

The furnace is worked without a *nose* on the tuyere.

Tin and slag collect in the fore-hearth, whence the slag is allowed to flow into a tank containing water, while the tin is tapped at intervals of 8 to 12 hours into the tapping pot; if the tin remains longer in the fore-hearth, hardhead separates out there.

When the furnace is working properly, the tin which runs from the furnace should be red-hot, and the charcoal visible through the tuyere hole should be at a yellow heat; if, however, the temperature rise too high, both the fuel visible through the peephole and the issuing tin will be at a white heat.

In 24 hours, 32 cwts. of ore and 16 cwts. of slag can be worked; from 7.2 to 7.8 cubic yards of charcoal are used for every 2 cwts. of tin produced. The loss of tin amounts to 12 or 15 per cent., of which 8 or 9 per cent. is due to volatilisation. The campaign lasts only 3 or 4 days. After the ore smelting, it is usual to follow on immediately in the same furnace with the treatment of rich slags and other intermediate products.

The slags contain unaltered tin ore as well as tin in the form of dross. This treatment yields slag-tin (*Schlacken-zinn*) and so-called *veränderte* slags containing still large quantities of tin. These are subjected to a further smelting (the so-called "*Schlackentreiben*") in blast furnaces.

The products of the ore smelting are crude tin, slag, and hardhead. The crude tin is refined (either by *boiling* or by liquating), the slags are further smelted to extract the tin they contain, and the hardhead, after a preliminary calcination, is added to the charge in the *verändern*.

At Graupen, in Bohemia,<sup>1</sup> ore is extracted from gneiss which carries from  $\frac{1}{2}$  to 10 per cent. with an average of 2 per cent. When this is dressed it yields coarse concentrates, tin ore containing from 68 to 72 per cent. of tin, and slimes with from 45 to 53 per cent. These are smelted in conjunction with ores from Bolivia, except when tin of special purity is required, in which case the concentrated ores are smelted by themselves. Ores which contain bismuth are previously roasted and treated with hydrochloric acid for the extraction of that metal.

The smelting of these ores is effected in the furnaces described and figured above, which are worked with a dark top and without *nose*.

<sup>1</sup> Balling, *Metallhüttenkunde*, p. 520.

Slags are added to the charge as a flux. After tapping, the tin is skimmed in the tapping pot and cast into bars. The slag which flows into the fore-hearth with the tin is from time to time lifted off and thrown into water. If the temperature rises too high, wet charcoal is used. In 24 hours, 22 to 24 cwts. of ore are smelted, using 13 cubic yards of charcoal. The slags contain 10 per cent. of tin.

The first smelting (*verändern*) of the slag, which is previously reduced to the size of peas, follows on the smelting of a parcel of ore. In this process a higher pressure of blast is used, and the diameter of the taphole is increased from  $1\frac{1}{2}$  inches to 3 inches. Further, on account of the greater fluidity of the slag from this operation, the tin is ladled from the fore-hearth; if it were tapped into the pot, the slag would run with it and would stop up the taphole. The slag obtained is quenched in water, crushed and smelted in the same furnace after the slag obtained from ore-smelting is finished. This second smelting of slag is called the *Treiben*. The products are tin and a twice-smelted slag which still contains tin mechanically enclosed in it; it is therefore stamped and washed, the portions rich in tin being added to the charges in a subsequent smelting of ore or slag. Furnace residues, old bricks, &c., containing tin, are also stamped and washed.

At Pitkaranta in Finland<sup>1</sup> tin-stone separated from copper ores and containing 55 to 65 per cent. of tin is smelted with charcoal in the shaft furnaces described above, the products being tin which is refined, and a rich slag containing 8.33 per cent. of tin mechanically enclosed, 56.19 per cent. of tin as oxide, and 11.9 per cent. of iron. This is smelted with other tin-bearing bye-products and the slag run into spherical slag pots, where the tin settles out.

At Tras,<sup>2</sup> ores containing about 70 per cent. of tin are smelted in the Chinese draught furnaces described above, the charge consisting of alternate layers of ore and charcoal. The ore is moist when charged so as to keep the upper part of the furnace cool and to prevent the loss of ore by the draught. The small quantity of slag which forms is drawn off from time to time from the tin which collects in the pot. In 24 hours 12 cwts. of metal are produced with a fuel consumption equal to the weight of the ore smelted. Each furnace is attended by 2 to 3 men. If the slag contains unreduced ore it is put back into the furnace; otherwise it is crushed and washed after a sufficient amount has collected, the tin particles collected, and the rest smelted again with charcoal. This operation follows, if possible, immediately after the smelting of the ore. The slag produced is again crushed, washed and smelted, and the resulting slag sold to special slag

<sup>1</sup> *The Min. Ind.*, 1896, p. 543.

<sup>2</sup> *Ibid.*, p. 546.

smelters. The tin content of the slags from the ore-smelting is given by Louis as 30 per cent.

In the Chinese blast furnaces at Dreda,<sup>1</sup> 1250 to 1670 lbs. of ore are worked off every 24 hours with a fuel consumption of 600 to 750 lbs. of charcoal and an output of 800 to 960 lbs. of tin.

In the Perak district of the Malay Peninsula, the output of tin in the newer furnaces figured above is 26 cwts. in 12 hours, the same weight of fuel being used. The slag is crushed and washed, the tin recovered in this way is re-melted, and the slag is smelted with charcoal in shaft furnaces, yielding thereby tin and another slag which is similarly treated. The third slag obtained in this way is sold to slag smelters, who smelt it again and crush and wash the slag produced from this operation in order to win the mechanically enclosed metal. The washed slag is oftentimes re-smelted.

According to Louis<sup>2</sup> the average yield of tin in the Malay Peninsula is 65 per cent. of the weight of the ore, so that as the ores average 69 per cent. of tin, the loss of metal may be placed at 6 per cent. The crude tin is refined in Singapore and Penang.

In Banca the ore is first dressed and then smelted in the three-tuyered furnace, 9 feet 3 inches high, described above. The smelting continues during 12 to 16 hours, being discontinued in the daytime on account of the excessive heat. In the 12 to 16 hours 3 to 4 tons of ore are treated, for which 30 to 38 cwts. of wood charcoal are required. The following may be quoted as the results of several nights' work<sup>3</sup> :—

TABULATED RESULTS.

Night.	Furnace No.	Date.	Time.			Ore smelted.		Charcoal used.	Tin obtained.		Tin per cent. of dry ore.
			From p.m.	To a.m.	No. of hours.	Lbs.	Moisture. Per cent.	Lbs.	Blocks.	Lbs.	
1st {	1	—	4	7.45	15½	9177	0.6	4342	66	4644	50.7
	2	—	4	8	16	9079	2.4	4322	72	4975	56.1
2nd {	1	2nd to 3rd Nov.	5.45	7.45	14	6881	1.1	3492	59	4097	60.1
	2		5.45	8	14½	6806	1.1	3492	58	4140	60.5
8th {	1	—	6	6.45	12½	7018	2.6	3411	58	4142	60.3
	2	—	6	6.45	12½	7061	2.5	3492	59	4262	61.9

<sup>1</sup> *The Min. Ind.*, 1896, p. 549.

<sup>2</sup> *Ibid.*, p. 550.

<sup>3</sup> Communication by Herr Neeb, from the *Jaarboek v. h. Mijnwezen in Nederlandsch Oost-Indie*, 1878, part ii., pp. 29-99.

The smelting of slags and residues containing tin follows immediately after the ore smelting. The tin produced in Vlaanderen's furnace is less pure than that from the Chinese furnaces and needs refining.

The slags obtained in the above smelting of ore are subjected, immediately after the ore smelting, to a repeated smelting in the same furnace; a great part of the tin contained in them is thus extracted.

#### THE EXTRACTION OF TIN FROM THE INTERMEDIATE PRODUCTS AND DROSSES OBTAINED IN THE TREATMENT OF TIN ORE.

In the production of crude tin from tin ore the following intermediate products and drosses are obtained, viz.:—slag containing tin, hardhead, and the scum formed on the surface of the bath of metal in the tapping pot after the tin has flowed from the furnace: also flue dust and furnace refuse (*e.g.* old bricks, &c., which carry tin).

The *Slags*, which are described in more detail on p. 522, require, as described above, further treatment in shaft furnaces, this treatment being called *Schlackenverändern* or *Schlackentreiben*. If they contain much enclosed metal, they are crushed and washed. The slags from the first treatment are dressed when worth it, and either smelted again or added to ore or other slag smelting charges. The tin recovered from the slags (*Schlackenzinn* or slag-tin) is at least as pure as that from the ores.

The first smelting of slag (*Verändern*) takes place usually immediately after the ore smelting, and in the same furnace. The smelting of the slag obtained from the first smelting, the so-called *Treiben*, is performed in the same furnace immediately on the conclusion of the first smelting, or in special shaft furnaces, known as *Treiböfen*. The slag from the *Treiben* is either thrown away, or if sufficiently rich in tin, submitted to a dressing process. These furnaces in Saxony and Bohemia are *Spuröfen*, and are of less height than the ore furnaces, in order to prevent as far as practicable the reduction of iron. Those in Saxony are 5 feet 6 inches high, and have a depth (*i.e.* from back to front) at the top of 2 feet 10 inches, and at the bottom of 2 feet 4 inches. The cross-section of the cavity is trapezoidal in shape, the front and back walls being parallel. At the mouth, the front is 1 foot 6 inches wide, and the back 2 feet 3 inches: at the bottom of the cavity the front is 1 foot 3 inches, and the back 1 foot 7 inches in width.

Other residues and drosses from the treatment of tin ore and from the refining are added to the slags when the latter are smelted.

A higher pressure of blast is used in smelting slag than in smelting ore.

The so-called hardhead, the tin-iron alloy referred to above, is obtained in slag smelting in addition to slag and tin.

The composition of a slag produced by slag smelting at Schlaggenwald in Bohemia, is given in the following analysis by Lill<sup>1</sup> :—

SiO <sub>2</sub>	. . . . .	24·06	per cent.
WO <sub>3</sub>	. . . . .	24·03	„ „
SnO <sub>2</sub>	. . . . .	10·41	„ „
FeO	. . . . .	20·75	„ „
MnO	. . . . .	5·64	„ „
Al <sub>2</sub> O <sub>3</sub>	. . . . .	9·00	„ „
CaO	. . . . .	3·50	„ „
MgO	. . . . .	0·37	„ „
		<hr/>	
		97·76	

Berthier gives the following as the composition of a slag from the second slag smelting at Altenwald in Saxony :—

SiO <sub>2</sub>	. . . . .	27·5	per cent.
SnO <sub>2</sub>	. . . . .	6·3	„ „
WO <sub>3</sub>	. . . . .	3·0	„ „
FeO	. . . . .	48·2	„ „
MnO	. . . . .	1·5	„ „
CaO	. . . . .	3·4	„ „
MgO	. . . . .	1·6	„ „
Al <sub>2</sub> O <sub>3</sub>	. . . . .	8·5	„ „
		<hr/>	
		100·0	

In Banca the slag produced by smelting ore is smelted with dross in the above described Van Vlaanderen's furnaces immediately after the conclusion of the ore smelting; for example, there would be smelted in two furnaces of that type in 12 hours<sup>2</sup> :—

186	lbs.	dry tin refuse.		
2077	„	damp tin refuse containing 5·51 per cent. of moisture.		
12552	„	stamped slag	„	5·51 „ „
7724	„	coarse „	„	3·44 „ „

These would consume 7060 lbs. of charcoal and would yield 78 blocks of tin weighing 5475 lbs.

The slag obtained from this first slag smelting would be again

<sup>1</sup> *Jahrb. der K. K. Berg-Academie*, vol. xiii., p. 64.

<sup>2</sup> Neeb, *loc. cit.*

smelted in the same furnace with refuse, producing tin and a third slag. The charge would be :—

7 lbs. dry tin dross.				
96	„	damp tin dross containing	1.79	per cent. of moisture.
1145	„	„ fine slag	20.35	„ „
1089	„	„ coarse slag	2.6	„ „

This would yield 236 lbs. of tin.

The third slag obtained from the above treatment would yet again be smelted for the extraction of its tin :—

9 lbs. dry tin dross.				
65	„	damp tin dross.		
418	„	fine slag containing	6.25	per cent. of moisture.
680	„	coarse slag	9.0	„ „

which would yield 486 lbs. of tin.

The fourth slag resulting from this last treatment would be stamped and concentrated by washing, the concentrated slag being smelted in smaller furnaces with tin drosses and richer concentrated slags from earlier smeltings. The fifth slag resulting from the above process would be again smelted after being stamped and concentrated. The sixth and last slag thus obtained would be thrown away even though it were not quite free from tin. The treatment of shaft furnace slags in the Malay Peninsula is continued as described above, until the tin content is brought down to 2 per cent.

*Hardhead*, the tin-iron alloy which is formed in the smelting of both ore and slag, has already been mentioned at page 478. This is added in the process of slag smelting, especially in the *Treiben* process; it is usually heated strongly with charcoal and suddenly quenched before smelting.

*Skimmings*, formed during the pouring of tin, are added during the smelting of ore or slag.

*The dust and furnace refuse* are also smelted with slag; they are usually put through a process of washing before being smelted.

#### *b. The Reduction of Tin Ore in Reverberatory Furnaces.*

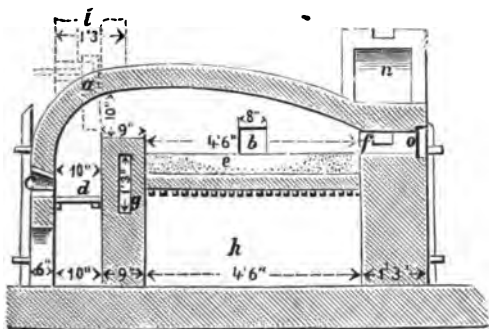
Reverberatory furnaces are or have been used for the smelting of tin ore in England, Australia, France, Spain, Germany, Mexico, California, and in the Malay Peninsula and in the island Pulo Brani.

The furnace consists of an elliptical bed, from 4 feet 6 inches to 12 feet in length, and from 3 feet 3 inches to 8 feet in greatest

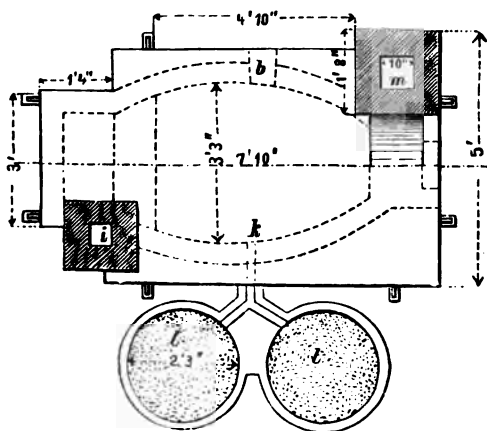


width. The bed is made of fire-clay, sand or fire bricks. In recent times the smaller furnaces have given place to larger ones.

The construction of a small furnace, with a bed 4 feet 6 inches in length, and 3 feet 3 inches in width, is shown in Figs. 409 and 410; *e* is the bed, *b* the working door at which the ore is charged, *o* the



**FIG. 409.**



**FIG. 410.**

working door at which the slag is drawn. The bed is supported by a grid of iron bars, under which is the *vault*  $h$ , which serves to keep the bed cool:  $d$  is the fire-grate with the fire-door,  $c$ ;  $g$  is the fire-bridge, through which a channel is built to keep it cool;  $f$  is the opening by which the flame leaves the furnace;  $n$  is the flue and  $m$  the chimney;  $i$  is a subsidiary stack connected with the fireplace by the opening,  $a$ , in the roof, into which the products of combustion are led while the furnace is being charged, in order to prevent the

fine ore being drawn into the chimney; *k* is the taphole, which is connected on the outside of the furnace with the kettles, *l, l*, for receiving the metal.

The construction of a larger furnace is shown in Figs. 411 and 412; the bed of this one is 12 feet in length and 8 feet in width.

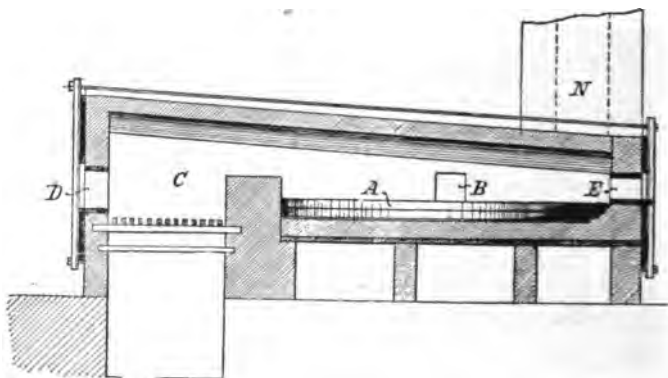


FIG. 411.

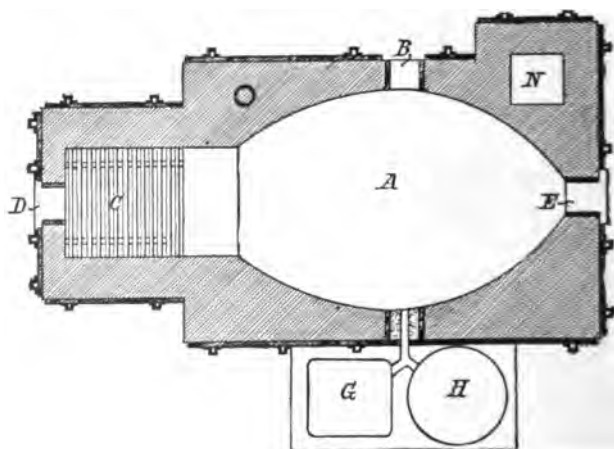


FIG. 412.

*A* is the bed, *B* the charging-door, *E* the door for drawing the slag. *C* the fire-grate with fire-door *D*. *G* is the kettle or float for receiving the tin, and *H* is a cast-iron kettle, heated by a separate fire underneath, which serves to receive the metal when the crude tin is refined by liquation in the same furnace; it is also used to contain the liquated metal while it is being *boiled*. *N* is the stack.

built and bound in with the furnace, and connected with it by an inclined flue. The kettle for receiving the metal when the furnace is tapped is lined with fire-clay. The arrangement of a furnace used in Lancashire<sup>1</sup> is shown in Figs. 413 to 415, Fig. 413 representing a longitudinal section of the furnace, Fig. 414 the plan, and 415 a section along the line *AB* in Fig. 414. The bed rests on cast-iron pillars, and is 14 feet 6 inches long by 9 feet 3 inches extreme breadth.

The latest Cornish furnace, with bed 14 feet 4 inches to 18 feet long and 8 feet to 12 feet wide, is shown in Figs. 416 to 419.<sup>2</sup> Fig. 416 represents a section along *CD* of Fig. 418; Fig. 418 the longitudinal section through the middle of the furnace; Fig. 419 the section along *AB* of Fig. 416; and Fig. 417 a section through the grate. The bed and the hollow fire-bridge are supported on iron bars, so that they can be cooled by the circulation of air beneath them. Air-holes in the side walls of the cavity enable this circulation to take place. On the iron bars rest slabs of slate or, less frequently, tiles of fire-clay, upon these a layer of clay 6 to 8 inches thick, and above all the bed proper. This is made of fire-brick and lasts about three months. A sloping floor of fire-brick under the hearth serves to collect the tin which percolates through the bed and convey it to an iron collecting pot *K*. The bed slopes from the short sides towards the middle, and then towards the tap-hole, which is placed at the front of the furnace in one of the longer sides. The tapping pot stands in front of the tap-hole, and the refining pot is at the side. Opposite to the tap-hole is the charging door, and the working doors are opposite to the grate. There is a clinker bed in the grate upon which coal is spread until it reaches the upper end of the fire-bridge. Each furnace has its own stack, which is about 50 feet high. In the figures, *A* represents the furnace arch made of fire-brick, *B* an air-hole for cooling the bed from below, *C* an air-hole for cooling the neighbourhood of the fire-grate, *E* the charging openings for fuel, *F* the same for the charge, *G* are openings for the removal of solid bodies from the bed, *H* the working doors, *K* the pot for collecting tin escaped from the bed, *L* the cast-iron refining pot, *Q* the tapping pot, and *R* the floor for gathering tin which may run through the bed. The charge is from 2 to 3 tons.

At Villeder in France a furnace has the following dimensions:—length of bed 11 feet, greatest breadth 6 feet 6 inches, and height of arch above bed 1 foot. The charge is 1½ tons of ore. At the Mount

<sup>1</sup> *The Min. Ind.*, 1896, p. 575.

<sup>2</sup> *Ibid.* p. 565.

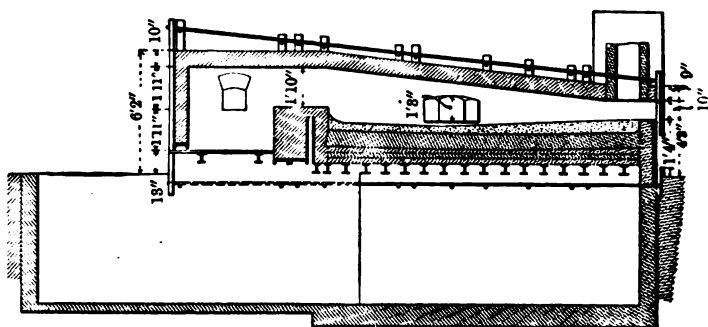


FIG. 413.

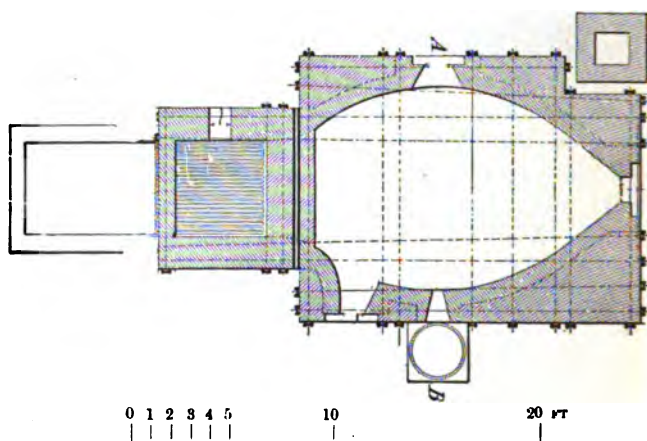


FIG. 414.

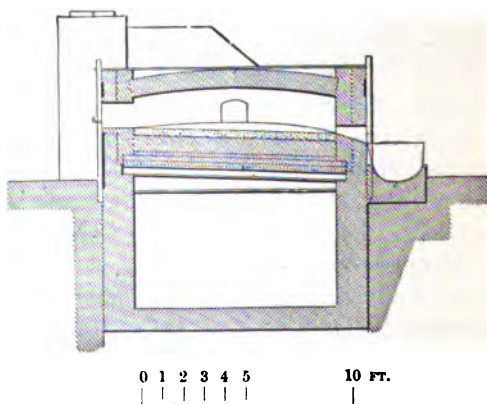


FIG. 415.

Bischoff works, Launceston, Tasmania, the beds are 13 feet 3 inches long and 9 feet 6 inches wide; the charge is 2.5 tons of ore.<sup>1</sup> At the

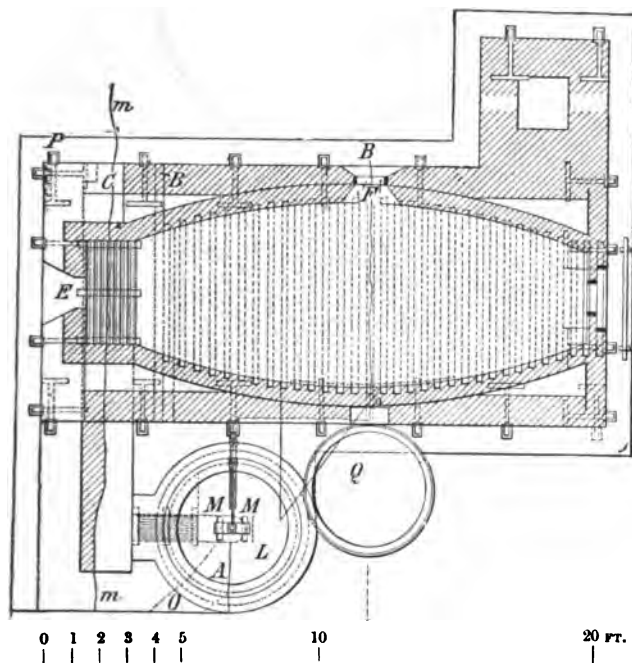


FIG. 416.

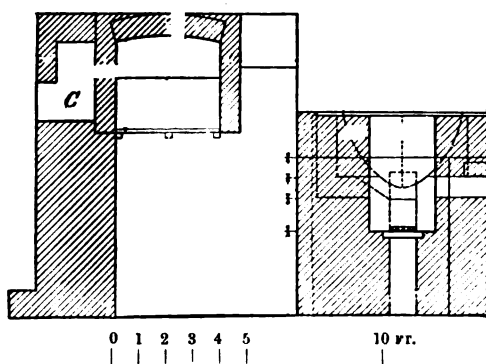


FIG. 417.

ent Hill works, New South Wales, the hearths are 14 feet to 16 feet long and 6 feet to 8 feet wide, the fire-bridge is 1 foot high and the chimneys 48 to 58 feet high; the charge of ore is 3 tons.

<sup>1</sup> *The Min. Ind.*, 1898, p. 649.

On the island of Pulo Brani, which lies west of Singapore, there are 14 furnaces working, each of which takes a charge of  $\frac{1}{2}$  tons. So far as construction is concerned they are the most modern of tin

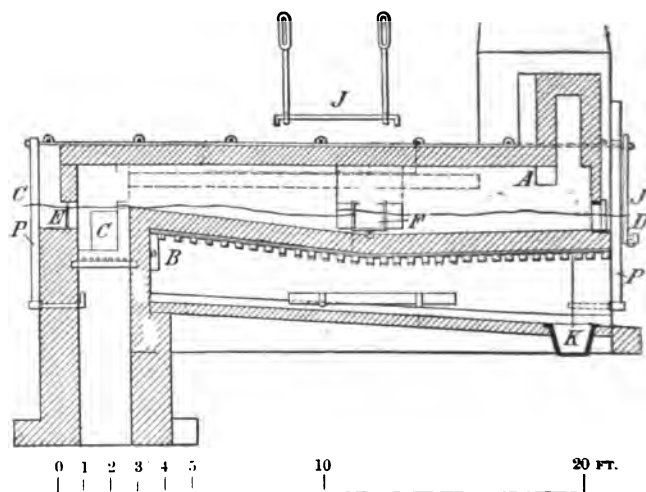


FIG. 418.

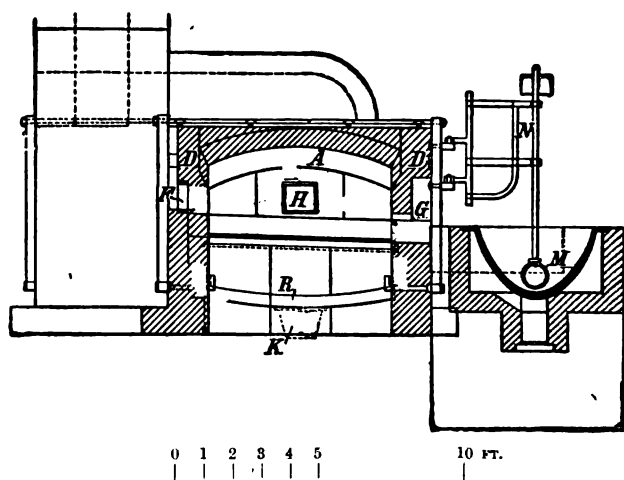


FIG. 419.

smelting furnaces. They are represented in Figs. 420 to 426.<sup>1</sup> Fig. 420 shows in the left half the view of the back end of the furnace.

<sup>1</sup> McKillop and Ellis. Tin Smelting at Pulo Brani. Excerpt from "The Metallurgy of Tin," 1895 and 1896. Part iii. "The Metallurgy of Tin," by Henry Louis. *The Min. Ind.*, 1896, p. 533.

the right half the front end; Fig. 421 is the side view, Fig. 422 is the horizontal section along *AA* and *BB* of Fig. 423; Fig. 423 is the longitudinal section through the middle of the furnace; Fig. 424 in the left half is a cross section along *DD* of Fig. 423, and in the right half along *CC* of the same figure; Fig. 425 shows the plan of the furnace top, and Fig. 426 a section along *EE* of Fig. 423. Under the

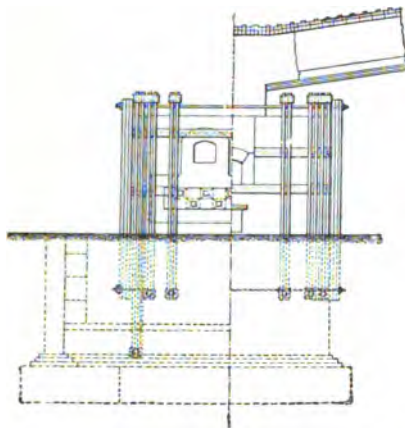


FIG. 420.

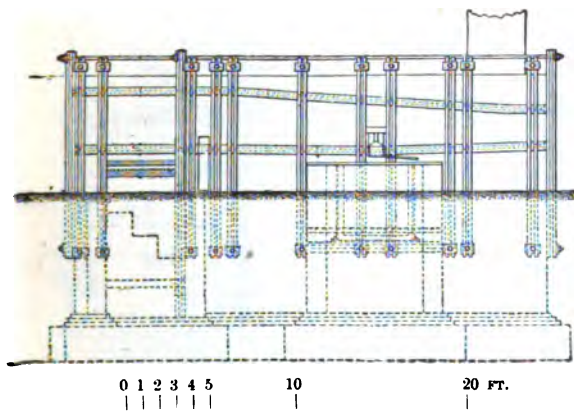


FIG. 421.

of the furnace is a vault containing water about 8 feet deep, into which the tin which passes through the bed drops and is granulated. At this depth of water no explosions take place. The water is changed out once a week in order that the granulations may be effected. The steam which is generated in this chamber escapes through two bent pipes 1 foot 6 inches in diameter placed at the stack-

end of the furnace. The hearth is built of firebrick and slopes from all sides to the tap-hole, which is placed at the long front side of the furnace. The length of the bed is 16 feet, the greatest breadth 9 feet 9 inches, and the breadth at the fire-bridge 6 feet. It rests on

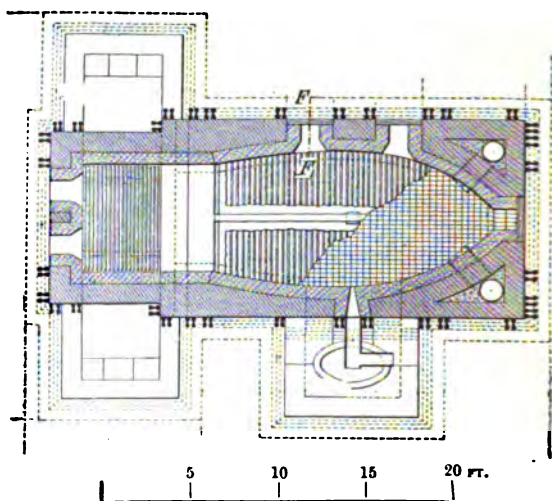


FIG. 422.

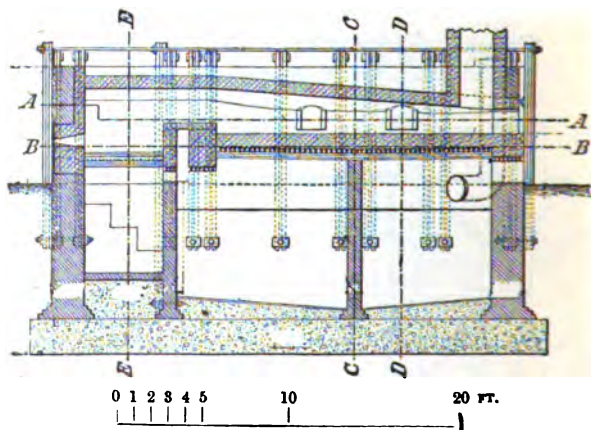


FIG. 423.

iron rails laid parallel to the short sides of the furnace. At one end these rails rest in the long side walls, at the other end they are supported on a long rail cut into halves, each half resting at one end in the furnace wall, and at the other end on a pillar in the middle of the furnace. When the bed, which lasts out 120 to 150 charges of



ons each of ore, needs renewing, this pillar is withdrawn so that the ed and its support fall together. The fire-bridge, which is 6 inches above the bed, is hollow and rests likewise on rails ; its upper edge is

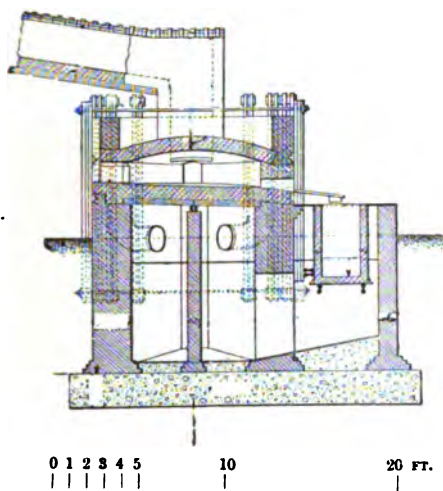


FIG. 424.

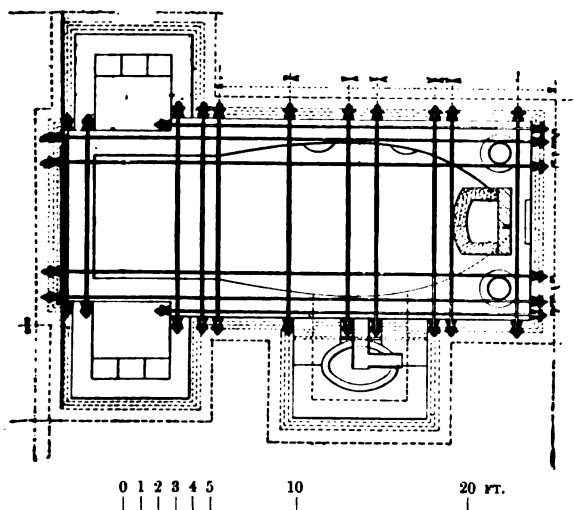


FIG. 425.

et 4 inches above the fire-grate. The size of the grate depends the nature of the fuel and varies between 4 feet by 6 feet and 4 t 4 inches by 6 feet 9 inches. The coal is charged in through two

openings on to the grate, the charge proper through two doors in the back wall of the furnace. The working doors are on the fore-side of the furnace.

The process is generally carried out as follows:—

The ore before it is charged into the furnace is mixed with non-caking coal or anthracite, as low as possible in ash, and sometimes with a small quantity of lime or fluorspar to flux the constituents of the ash of the coal. The mixture is wetted to prevent the dust being

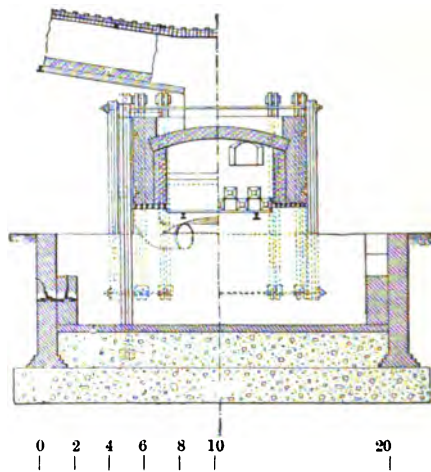


FIG. 426.

carried away during charging, and thrown on the bed through the charging door, after which it is levelled from both working doors.

The normal working of a charge is as follows:—First, the doors being shut, a gradually increasing fire is applied. After a time the fused mass is thoroughly stirred, this being done through the slag door, the position of which under the chimney prevents the stream of air which rushes in from coming in contact with, and oxidising, the tin. After this a strong heat is applied for a further period, and the charge is again stirred. The reduction of the tin, as well as its separation from the slag, should now be complete. The slag is now either skimmed off from the metal through the slag door, after being stiffened by the addition of fine coal, and the tin is run out with a small quantity of slag; or else both slag and metal are tapped together. In the latter case the slag is allowed to “set” on top of the metal in the pot, and then lifted off. The tin is now either cast into ingots or passed on in the liquid state to be refined. A sponge

mass of slag frequently remains on the bed after tapping : this retains mechanically a considerable quantity of tin prill ; it is drawn through the slag door, after which the furnace is again charged.

The whole process lasts from 6 to 12 hours according to the size of the charge and the quality of the ore and fuel.

The reduction of the tin-stone is brought about by the carbonaceous matter of the coal or charcoal added. The gangue and the coal ash form a slag, the formation of which is sometimes promoted by the addition of lime or fluorspar.

The products of this process are tin and slag. The tin, if derived from a pure ore, will be at once taken in the fluid state to be refined either in the boiling kettle or in a special refining furnace ; if it be impure it will be cast into ingots and subjected to liquation. The slags are silicates of tin and of the other metallic oxides contained in the ore ; they also contain tungstic acid if wolfram be present in the ore. Their constitution varies ; in most cases they are mixtures of mono- and bi-silicates, and contain mechanically enclosed prill as well as oxide of tin.

The following analysis gives the composition of ore slag examined by Berthier ; it had been run in a reverberatory furnace at Poullaouen, in France, from an ore from Piriac, and dressed tin dross :—

SiO <sub>2</sub>	. . . . .	40·0	per cent.
SnO <sub>2</sub>	. . . . .	8·4	„
FeO	. . . . .	20·3	„
MnO	. . . . .	11·1	„
CaO	. . . . .	3·6	„
MgO	. . . . .	1·0	„
Al <sub>2</sub> O <sub>3</sub>	. . . . .	9·6	„
		<hr/>	
		94·0	

A slag from Pulo Brani contained, in addition to magnesium, calcium, titanium, and manganese :—

Tin	. . . . .	35	per cent.
Silica	. . . . .	15	„
Aluminium	. . . . .	18	„
Iron	. . . . .	9	„

In Cornwall three sorts of slags are usually distinguished viz :—

(1) Poor slags which can be thrown away. (2) Richer slags containing mechanically enclosed prill, from which the richer portions

can be separated by a dressing process, to be afterwards smelted up with tin produced by smelting slag : and (3) the slag remaining on the bed after tapping, which contains a large quantity of prill ; this can be treated by smelting it with tin ore or with the rich product obtained by dressing the above mentioned second kind.

At Penzance the charges of ore in the modern furnaces described above are 2 and 3 tons, three 3-ton charges, and four 2-ton charges being worked off in 24 hours. The dressed ores contain 62 to 65 per cent. of tin and 5 to 6 per cent. of ferric oxide along with silica and other impurities, and these are worked along with Bolivian ores containing 72 per cent. of tin, 5 to 6 per cent. of silica, and 1 to 3 per cent. of ferric oxide. The ores are mixed with 15 to 20 per cent. of anthracite (culm) and a small quantity of slaked lime, along with tin-bearing slags and bye-products and a little fluorspar. The mass is moistened and introduced in the furnace still hot from the treatment of the previous charge, and is there raked to cover the bed. The doors of the furnace are closed and luted and the charge strongly fired. After 1 to 3 hours the mass has become molten and is then rabbled, this process being repeated from time to time if need be. After strongly heating from 5 to 7 hours the process is completed : the whole is then rabbled and allowed to stand so that the tin separates from the slag. The latter is stiffened if necessary with anthracite and removed as far as possible through the working doors by means of hooks. The upper layer of slag, which makes up about  $\frac{2}{3}$  of the whole, contains but little tin and is thrown away ; the lower layer, containing mechanically enclosed tin, is subjected to dressing. The rest of the slag is smelted along with the grains from the dressing operation. As it is impossible to withdraw all the slag from the furnace, part is tapped along with the tin and is lifted off from the metal in the pots after separation has taken place. This slag is called *glass*, and must be smelted again for the recovery of tin. Any spongy slag still remaining in the furnace is withdrawn through the working doors. The tin is allowed to cool in the tapping pot, the scums being removed as formed, and is poured into moulds. It is then refined. In 24 hours 16 men attend four furnaces, 4 charges are worked off in each furnace in 24 hours, and 2 tons of fuel are consumed for 1 ton of ore. The total loss of tin, inclusive of the slag and bye-product treatment, is given in Cornwall as 9 per cent. of the tin content of the ores.

At Villeder, in France, where the furnaces are 11 feet in length on the bed, with a width at the widest part of 6 feet 6 inches, the charge consisted of  $1\frac{1}{2}$  tons of ore and 6 cwt. of anthracite, and was

smelted in 8 hours. In 24 hours, 6 tons of ore were worked with a consumption of 9 tons of coal, exclusive of the anthracite mixed with the charge.

At the Mount Bischoff works in Tasmania, Cornish furnaces, 13 feet 3 inches long by 9 feet 6 inches in extreme width, are in use for the treatment of ores,  $\frac{3}{4}$  of which came from the Mount Bischoff mines; the remainder is alluvial ore from the east coast of Tasmania. The local ore contains 65 to 72 per cent. of tin and is contaminated chiefly by iron, the alluvial ore contains 70 per cent. of tin and is siliceous, and these are so blended that the iron of the one is slagged off by the silica of the other. The charge consists of 2.5 tons of the ore and 0.5 ton of small coal. This is charged into the furnace through the two doors, the bed of the furnace being strewn with tin dross and scrap metal. The doors are closed and luted on, the furnace is fired strongly, and the mass is thoroughly rabbled 3 or 4 times. As soon as the well-molten mass has settled, the tin is tapped into the pot, and the residual slag, after strongly firing for another hour, is run into sand moulds. The whole process lasts 8 hours. The tin in the tap-pots is allowed to cool an hour and is then ladled into refining kettles, where it is poled. The slags contain 10 to 20 per cent. of tin, and are submitted to a slag-smelting process to be described later. The fuel consumption per ton of ore, inclusive of slag treatment, is 1.02 tons of coal.<sup>1</sup>

At the Tent Hill works in New South Wales,<sup>2</sup> wood is the fuel used. The beds are 14 to 16 feet long and 6 to 8 feet wide, the charge consists of 3 tons of ore and 1 ton of moistened charcoal, and the treatment lasts 12 hours; the tin, after cooling in the tapping pot, is ladled into a refining pot and there poled. The slags are smelted again.

In the furnace at Pulo Brani<sup>3</sup> described above, the charge is 4 tons of ore, made up according to the tin content. With ores containing from 65 to 71 per cent. of tin, the charge averages 80 parts by weight of ore, 10.4 of culm, and 2.4 of refinery dross; when the ores contain more than 71 per cent. of tin the charge is made up of 80 parts of ore, 12 parts of culm, and 2.4 of refinery dross. If the coal, which is used as fuel, is of good quality, the mass is rabbled after 2 to 2½ hours' firing; otherwise it must be heated an additional 1½ hours. The mass is then fluid at the fire-bridge and pasty in the middle of the furnace. After the first rabbling, it is strongly heated an hour and again rabbled; it is then quite molten and free from solid lumps on the surface. It is again strongly fired and the tin tapped in a

<sup>1</sup> *The Min. Ind.*, 1898, p. 649.

<sup>2</sup> *Ibid.*, 1896, p. 576.

<sup>3</sup> *Ibid.*, p. 585.

fine stream by partly opening the tap-hole. The tapping takes up  $\frac{3}{4}$  hour, after which the hole is plugged, a gutter is placed to connect it with a sand bed, and the hole is fully opened, so that the slag flows in full stream to the sand bed. A charge is worked off in  $7\frac{1}{2}$  to 8 hours, the products being *ore metal* containing 99.5 per cent. of tin, which after cooling is run into moulds and refined, and a slag with 20 to 40 per cent. of tin, which is smelted again. The fuel consumption per ton of ore inclusive of slag-smelting and refining is 0.98 ton of coal.

At the Temescal Mines in California tin ores used to be smelted in Cornish furnaces, petroleum being used as fuel.<sup>1</sup> The furnaces were 11 feet long by 10 feet 6 inches wide; the charge consisted of 18 cwt. of ore, containing 65 per cent. of tin, mixed with 20 per cent. of its weight of coal, and 3 charges were put through in 24 hours. The slags containing 5 per cent. of tin were crushed and washed. The operations have long been stopped owing to the high cost of working the ore deposits.

At the Tostedt works on Lüneburg Heath (Kreis Haaburg). Bolivian ores containing 40 to 60 per cent. of tin and 10 to 30 per cent. of silica are roasted and then smelted in reverberatory furnaces. There are four Cornish furnaces, two small and two large ones. The former put through 4 to 4.3 tons of ore in 24 hours, the larger 6 to 6.6 tons. The ore is charged in with 15 to 20 per cent. of finely ground anthracite, and with 50 per cent. more lime than is needful to slag off the silica. Each charge requires 8 to 10 hours' treatment in the furnace; the fuel used is 50 per cent. of the charge for the large furnaces and somewhat more for the small ones. Two men per shift attend the small and three men the large furnaces. The hearth is made of sand and lasts a month. The tin is tapped into a cast-iron pot and is then liquated and poled; the slags are run into a sand bed. They contain 20 to 25 per cent. of tin, and are submitted to further smelting operations.

*The Treatment of Intermediate Products and Dross obtained by the Reduction of Tinstone in Reverberatory Furnaces*

The bodies included under this head are slags, hardhead, skimmings, and furnace accretions.

The *Slags* contain tin as silicate and in the metallic state mechanically enclosed as prill. These are treated in the dry way except at Tostedt, where wet methods have also been employed.

<sup>1</sup> *The Min. Ind.*, 1896, p. 587.

(These will be described in a later chapter on the extraction of tin in the wet way.) For the recovery of tin from slags containing it as silicate two methods are employed, viz., the reduction and the precipitation methods.

The *reduction* method consists in smelting the slags in reverberatory furnaces with coal and a stronger base than tin oxide, so that this base (usually lime) replaces the oxide of tin and the latter is reduced to metallic tin.

The *precipitation* method consists in smelting the slags with iron, which decomposes the silicate of tin, forming tin and ferrous silicate. The iron is used in the form of scrap, or alloyed with tin as hardhead. Tin oxide mechanically enclosed in the slag is reduced by coal. As slags always contain tin oxide in this condition, and as, furthermore, dross containing the oxide is added to the smelting charge, coal must always be added in the precipitation method. The metal present as prill is either recovered by grinding and washing the slags or by fusing them and allowing the tin to settle out. Slags containing less than 5 per cent. of tin are generally thrown away in Cornwall. The reverberatory furnaces used in slag smelting are the same as those used in smelting the ore; sometimes shaft furnaces are employed.

In Cornwall the first slags (about  $\frac{1}{3}$  of the whole) drawn from the surface of the metal in the ore reduction are thrown away; the following layers which contain grains of tin are crushed and washed to recover the tin, and the residual slag, along with the slag from the tapping pots and the tin recovered by washing, is mixed with coal and lime and treated by the reduction method. Refinery dross and other intermediate tin-bearing products are also added to the charge to be smelted. The products are tin, which is refined, and slag, which is added to slag smelting charges or is smelted by itself, unless it contains under 5 per cent. of tin, in which case it is thrown away.

At Pulo Brani the slags from the ore-smelting contain from 20 to 40 per cent. of tin; they are treated by the precipitation method in reverberatory furnaces of the same construction as those used in smelting ores, the operation generally following immediately upon the ore-smelting as with the increased heat required in the treatment of slags cracks in the bed are readily filled with slag. The slags to be smelted are mixed with scrap-iron, limestone, refinery dross, and anthracite, the best mixture containing 30 parts by weight of slag, 12 of dross, 2.75 of iron, 2.4 of limestone (coralline), and 6 of culm. The charge weighs 4 tons. After melting down it is well rabbled, heated strongly an hour and tapped, the tin into a tapping pot, the slag into moulds. The whole process of smelting lasts 7 hours, and

the products are "rough metal" containing 95.5 per cent. of tin, and "poor slag" which contains at least 2.5 per cent. of tin as silicate and up to 10 per cent. as prill. The silica content averages 60 per cent. The prills are only found in the layers immediately above the tin; these constitute  $\frac{1}{3}$  of the whole slag. The rest of the slag is tested for prills, and if absent, it is thrown away. To prevent the formation of hardhead the rough metal is run from the tapping pot into moulds and kept stirred with an iron rod so long as it remains liquid. This end may also be attained by granulating the metal. The crude metal is liquated and then refined. The slag containing prills is crushed and washed, but as the grains of tin are brittle owing to impurities and are thus easily washed away in a finely divided condition, it is preferable to smelt the slag in a reverberatory furnace with lime and anthracite, as is done at Pulo Brani. The effect of this is to combine the separate grains into one mass, which collects on the bed of the furnace, and to reduce the tin present as silicate by the coal which is added.

The charge consists of 40 parts by weight of slag, 2.5 of limestone, and 2.5 of culm. If the slag is free from silicate, limestone and coal need not be added. The weight of the charge is 4 tons. It is rabbled from time to time, first after 2 hours' heating, and then again after another hour, the whole process lasting 5 to 6 hours. The metal is allowed to collect on the bottom of the furnace bed and is tapped thrice a week into sand moulds. It contains 80.5 per cent. of tin and 19.5 per cent. of iron, and is submitted to repeated refining. The tin obtained in Pulo Brani from 100 parts by weight of charge is distributed as follows among the various products:—ore metal from the smelting of the ores 58 parts, containing 57.7 parts of tin; rough metal from the first slags 9 parts, containing 8.6 of tin; metal from the smelting of the poor slags 2 parts, containing 1.6 of tin, *i.e.*, altogether 67.9 parts by weight. The worthless slags constitute 27 per cent. of the weight of tinstone and contain 5 per cent. of tin; the consumption of iron is 4.7 per cent., that of culm 27 per cent. of tin produced. If the ores contain 70 per cent. of tin, the loss by slagging off is calculated at 2 per cent. only. The consumption of coal is 0.98 ton per ton of ore.<sup>1</sup>

At the Australian works<sup>2</sup> the slags from the ore smelting are also smelted with additions of iron. At the Tostedt works, slags from the

<sup>1</sup> "The Metallurgy of Tin." H. Louis. *The Min. Ind.*, 1896, p. 583. The smelting at Pulo Brani, McKillop and Ellis in Excerpt, Minutes of *Proc. Ind. Cir. Eng.*, 1895 and 1896. Part iii.

<sup>2</sup> *The Min. Ind.*, 1896, p. 576; 1898, p. 649.



ore-smelting containing 20 to 25 per cent. of tin are smelted in the reverberatories described above with 6 to 8 per cent. of hardhead (the tin-iron alloy left on liquating tin). The products are tin and slag. The latter is mixed with 6 to 10 per cent. of hardhead and 15 to 18 per cent. of coke, and smelted in 3-tuyered shaft furnaces 30 feet high and 7 feet in diameter at the boshes, 20 to 24 tons of slag being put through in 24 hours. Tin and slag are thus obtained, and the slag is smelted once or twice again in the shaft furnace. The clean slags contain less than 5 per cent. of tin.

Hardhead, dross, flue-dust, furnace accretions, and broken furnace beds are smelted along with the slags.

### I. B. THE REFINING OF TIN

The tin obtained by the processes described above, known as crude or raw tin, is usually impure and carries different metals, *e.g.*, iron, copper, lead, antimony, and arsenic, which deteriorate it. It therefore requires to be freed from these impurities by a process of purification, the so-called refining. This purification consists of either a liquation of the tin or a liquation followed by *boiling* or *tossing*. In the case of a very pure tin, it is only boiled or melted and allowed to stand.

In the liquation the pure tin is melted out, while the impurities which are less fusible than the tin remain behind in the form of alloys, known as *liquation-dross*. In *boiling* and *tossing* each portion of the melted metal is brought into contact with the air and the more easily oxidisable metals thereby separated as oxides. When tin is re-melted and allowed to stand, the impurities separate out partly at the surface in the form of dross, and partly sink alloyed with tin to the bottom of the pot.

#### a. The Liquation of Tin (*Pauschen*)

The liquation ("*Pauschen*"), or flowing ("*Flössen*"), of tin is done in hearths, pans, and reverberatories. Liquation hearths are used in Saxony, Bohemia and Billiton. In Saxony and Bohemia the liquation is done immediately after the metal has been tapped from the fore-hearth into the tapping pot, the so-called liquation hearth being used for the purpose. This is an inclined plate of cast-iron with ridges on it, covered with clay; it is 3 feet 7 inches long and 2 feet 4 inches broad, resting on masonry, with a cast-iron pot placed at its lower end. The slope of the plate is 1 in 7 to 1 in 10 and it

is placed at the front end side of the shaft furnace near to the tapping pot as shown in Fig. 427; *e* is the hearth of the shaft furnace, *g* the forehearth, *h* the tapping pot, *v* the liquation hearth, and *z* the pot for the reception of the liquated tin. When in use, this plate is covered with a layer of glowing charcoal, and the tin is taken from the tapping-pot with a ladle and poured over it; the less fusible alloys remain behind while the purer metal runs off the inclined plate and collects in the pot at its lower end, this being also filled with burning charcoal. It is again ladled out of the pot and poured over the fuel on the plate, and this is repeated until it no longer leaves a residue behind it in passing over the plate.

After this, the residues on the plate are all collected together and beaten with wooden hammers, by which process some tin is liberated

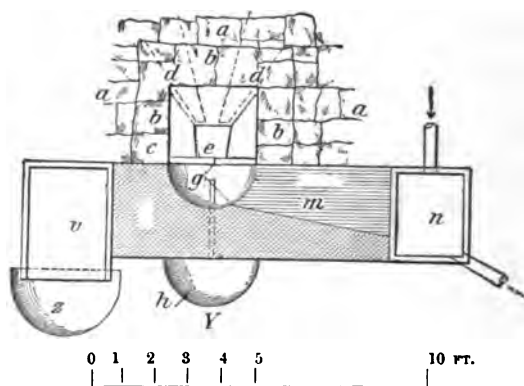


FIG. 427.

and runs into the pot, while the less fusible alloys, known as "*Saigerdörner*," remain behind.

The tin which has collected in the pot is allowed to cool there until it shows a bluish, brilliant surface, whereupon it is at once cast. It is either poured into moulds or on to a level, smooth, polished, copper plate from 4 feet 2 inches to 5 feet 2 inches long, 2 feet broad, and  $\frac{1}{4}$  inch thick. In the moulds it takes the form of ingots or bars; on the copper plate that of sheets  $\frac{1}{16}$  inch thick. These are taken when cold to a rolling bench, where they are rolled together and then beaten with wooden hammers. The rolled tin is known as *Rollenzinn* or *Ballenzinn*. The residues from liquation, called also *Zinnpausche* or *Zinnkörner*, are essentially a tin-iron alloy containing varying quantities of tungsten and copper. They are usually worked

up by adding them to the charge in slag smelting. The composition of liquation dross from Altenberg is shown in the two following analyses :—

	I. Lampadius. Per cent.	II. Berthier. Per cent.
Sn . . . . .	68·13	72·52
Fe . . . . .	25·49	26·44
W . . . . .	5·14	1·04
Cu . . . . .	0·74	—
	<hr/> 99·50	<hr/> 100·00

In the island of Billiton the liquation hearth consists of a sloping cast-iron plate set into three brick walls and having a couple of iron steps at the lower end under which is placed the pot for the reception of the liquated metal. Charcoal is strewn on the plate and made to glow by the blast from a tuyere in the back wall, and the tin is laid on the hearth in blocks either resting directly on the charcoal, or upon iron bars held a little above it. The liquated tin flows down the plate into the pot, and is cast from there into moulds.

Dijk<sup>1</sup> used a wrought-iron pan heated from below in order to liquate crude tin from Banca (with 1 per cent. impurities) obtained in the Vlaanderen shaft furnace. The arrangement is shown in Fig. 428. The ingots of zinc were laid upon a bed of charcoal on the bottom of the plate, which was fired from below. A pot placed in front served to collect the liquated tin. The first residues were further liquated at a higher temperature, and the two liquated products contained 99·84 and 99·79 per cent. of tin respectively. The only impurity in the metal was iron. The liquation residue contained 80·8 per cent. of tin and 19·2 per cent. of iron, and corresponded closely to the formula  $\text{FeSn}_2$ ; the loss by liquation was

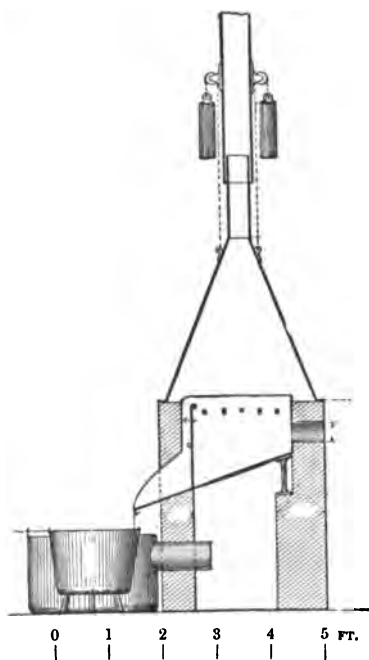


FIG. 428.

<sup>1</sup> *The Min. Ind.*, 1896, p. 559.

0.33 per cent. At present<sup>1</sup> the impure tin, which forms, however, only one-tenth of that produced in Vlaanderen's furnace, is melted in iron pans in charges of 15,000 to 16,000 lbs., heating being done from above by a wood fire. As the metal melts it flows into a receiver of the same size as the melting pot, in which the less fusible tin-iron alloy remains behind; thence the pure tin passes on to a third pot holding 1,100 lbs., called the controlling pan, then into a fourth pan, from which it is cast in moulds. All the pans are embedded in sand, which retains any escaping metal. The alloy is removed from the second pan with perforated ladles, melted down in small shaft furnaces, and liquated on iron plates; the liquated metal is collected in a pot and cast into moulds. The residual alloy is regarded as worthless. The loss of tin amounts to 2 per cent.

#### *b. The Refining of Tin by the English Method*

The English method of refining consists of a liquation of the tin in a reverberatory furnace and a subsequent *boiling* or *tossing*. This method is employed in Cornwall and Lancashire, in Germany at Tostedt, and in Pulo Brani and in Australia. The operation of boiling and tossing will be considered after the description of the liquation process at these places.

In England the liquation furnaces are either especially constructed for the purpose, or they are the same as those used for smelting the ores. In the latter case they are fitted with kettles, separately fired, for the reception and boiling of the tin. (These kettles are shown at *H* and *L* in Figs. 412 and 416 respectively.) A special liquation furnace used in Lancashire is shown in Figs. 429 to 431. It consists of two cast-iron hearths, sloping in opposite directions, each with a separately fired collecting and boiling pot at the corresponding ends of the furnace. The block tin is laid upon the upper end of these plates and melted down slowly, the tin flowing through the tap-hole into a pot placed below, while the less fusible metals and part of the tin remain on the plate.

Fresh ingots are piled on the bed as those previously charged are liquated. When the pots, which hold 6 to 10 tons, are full of tin, the temperature is raised until the residue on the bed is melted, after which it is allowed to run into a separate pot; here the less fusible metals settle down to the bottom in the form of tin alloys, while the tin, which still contains small quantities of arsenic, sulphur

<sup>1</sup> Seventeenth Annual Report of the U. S. Geological Survey, 1895-96. Part iii. p. 239.

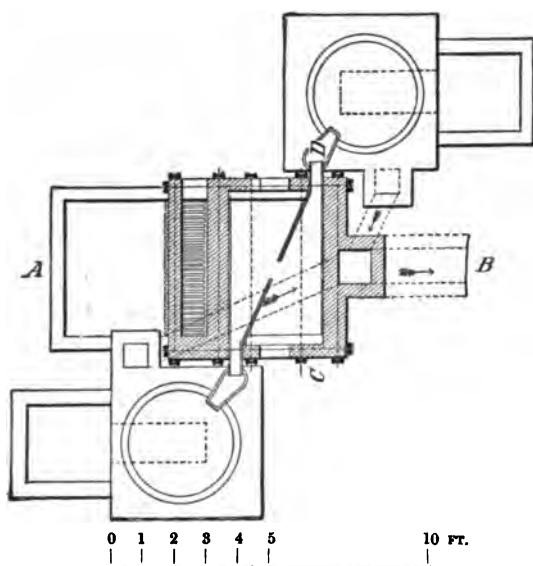


FIG. 429.

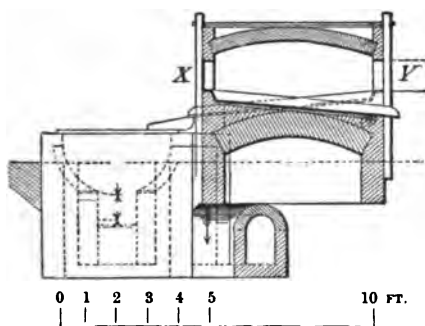


FIG. 430.

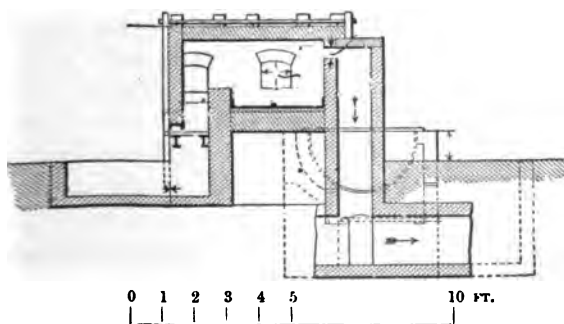


FIG. 431.

and iron, remains liquid. The tin is cast in moulds, and as soon as a sufficient quantity has accumulated, is again liquated.

The liquation dross and the residue on the furnace bed are once more liquated, after which the infusible portions are either added to charges of slag or thrown away.

The tin which collects in the refining pot (*kettle*), amounting to 6 or 10 tons at one time, is kept at a high temperature by means of a strong fire underneath, while it is being *boiled*, or more rarely, *tossed*.

The boiling consists in introducing into the bath of heated liquid metal a bundle of green twigs, held together by two iron bands. These are fastened by a cross-piece to a weighted iron bar which hangs from a chain and pulley. The wood, at the high temperature, undergoes a dry distillation, and the gases and vapour given off set up a bubbling action in the bath of metal. By this means every portion of the mass is brought into contact with the air, the foreign metals and a portion of the tin being oxidised. The oxides collect together in a foamy mass, the so-called *boil-scum*, on the surface of the metal.

The duration of the *boiling* depends on the state of purity to which it is desired to bring the tin; if a high degree of purity be required, the boiling must be continued for many hours. It is continued till the surface of the molten metal, after removal of the scum, is bright and shining, after which the metal is allowed to stand quiet for some time (one hour, more or less) in order that the heavy metals in the tin, especially copper and iron, may have an opportunity to settle to the bottom. After this, the scum is skimmed off and the metal ladled into moulds. The upper portions of the metal in the pot are the purest, the lower layers being only of common quality; the portions at the very bottom are usually liquated and boiled over again.

The tin from the upper layers in the refining pot, described as refined tin, goes to the market in the form of ingots or of *grain-tin*, in masses 7 to 100 lbs. in weight, or in strips 3 to 5 of which weigh 1 lb. Tin of second quality, either from the lower layers of metal in the refining pot—or produced by shorter boiling—goes by the name of common tin, and is sent into the market in ingots weighing 350 to 400 lbs. apiece.

*Tossing* is sometimes resorted to in England instead of boiling. To do this the workman continually takes up a ladleful of the melted metal and pours it back from a height into the pot. This method also allows every portion of the mass to be brought into contact with

the air. The products from *tossing* are the same as those from *boiling*.

The refining of 6 or 7 tons of tin requires altogether from 5 to 7 hours, viz.,

Liquation . . . . .	1 to 2 hours
Boiling according to the purity required . . . . .	3 „ 4 hours
Settling and pouring . . . . .	1 hour.

At Tostedt the liquation furnaces are rectangular, with fire-grate on the long side of the furnace, the hearth is sloping and divided lengthwise into three parts, the length being 18 feet, the width 8 feet. The ingots of tin are placed at the upper end of the middle division, and the liquated metal flows away at the lower end of this into moulds. It is taken from these to the division furthest removed from the fire, whilst the liquation residues from the middle division are transferred to the first division nearest to the fire. The tin liquated in the third division of the hearth is boiled. The liquation residues heated on the first division yield a little tin and the residue is withdrawn from the furnace; the residues from the third division are passed on to the middle division, as is also the tin from the first or hottest part of the hearth. In 24 hours 3 tons of tin are liquated in this furnace.

The tin is boiled in a cast-iron kettle holding  $6\frac{1}{2}$  tons. It is quickly melted, poled with green wood for  $1\frac{1}{2}$  hours, and then cast into moulds. Two charges are worked off in 12 hours. The best grades of tin contain 99.95 per cent. of the metal.

At Pulo Brani, near Singapore, the crude tin is liquated and ossed. If it is very impure it is boiled before liquating. The arrangement of the liquation furnace is shown in Figs. 432 and 433. The furnace is rectangular in cross section, with a grate at each end. Wood is the fuel used. The gases from the fire reach the middle of the furnace through a flue in the arch. The liquated tin flows away from the furnace through two open tap-holes into the pots *A* and *B*. Each kettle is 3 feet 6 inches in diameter and holds 3 tons of tin. It is ladled from these into one of the larger pots *C*, *D*, *E*, or *F*, each of which is 8 feet in diameter and holds 30 tons. The pots *A* and *B* are 2 feet higher than *C*, *D*, *E*, and *F*. During boiling, the tin falls from the ladle in a fine stream about 4 feet above the air. It remains in the pots 24 hours at a temperature of  $260^{\circ}\text{C}$ ., during which time the impurities, in so far as they do not form scums, settle to the bottom. After skimming, the metal is ladled out into moulds; that portion down to a foot from the bottom goes

into the market, the rest is liquated again. The liquation residues are added to ore charges. From 100 parts of crude tin from the ore-smelting, there are obtained 96·5 parts of refined tin and 4·5 to 5 parts of liquation residues and drosses. The liquation residues contain 65 per cent. of tin and 11·5 per cent. of iron.<sup>1</sup>

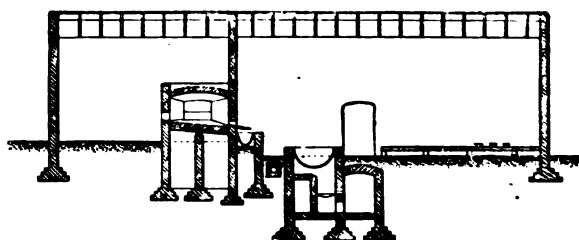


FIG. 432.

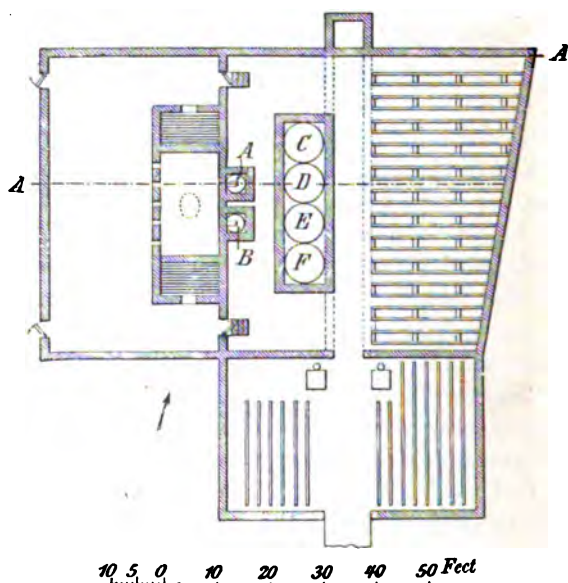


FIG. 433.

At Mount Bischoff works, Launceston, the tin from the ore-smelting process is only boiled, the operation lasting 2 to 4 hours according to the purity of the metal.<sup>2</sup>

In the Malay Archipelago, the refining process consists only in

<sup>1</sup> McKillop and Ellis, *op. cit.*

<sup>2</sup> *The Min. Ind.*, 1898, p. 649.



melting, stirring the molten tin, and allowing it to stand in order that the impure alloy may settle out. After skimming the tin is cast.

The tin produced in the Chinese furnaces at Banca is so pure that it does not need refining. It is at most remelted.

### *c. Purification of Tin by Filtration*

Repeated proposals to purify tin by filtration have been made, but so far have not been adopted.

The first proposal of this kind by Lampadius was to filter the tin through quartz sand, or finely divided slag, which was to be previously heated; the result, however, was most unfavourable.

Carter proposed a filter of thin tinned sheet iron, the sheets being about 6 inches long and 4 inches broad. Five hundred of these sheets were to be wedged into a square frame, which was to be fastened in an opening of corresponding size in the bottom of a Passau graphite crucible. When melted tin was poured on to this filter, the tin coating of the tin plate became fluid, and allowed a very pure tin to pass the filter, while a pulpy mass of arsenic, copper, iron, and tin remained behind. This proposal has found no practical application; neither has that of Leichsenring, by which the tin was to be allowed to run through sieves of coarse and fine iron wire.

Tin produced electrometallurgically is also impure and needs refining. To free tin from lead Borchers<sup>1</sup> has suggested smelting it with haloid salts of tin and the alkalis. He states that Peetz, working at the Technical High School of Aix-la-Chapelle, obtained good results by melting lead-bearing tin with the stannous potassium chloride, a double salt readily prepared and melting between 300° and 400° C.

*The products of the refining of tin* are:—Refined tin, liquation dross, and boil scum.

The composition of different qualities of pure tin is shown in the following analyses:—

	From Saxony. <sup>2</sup>		From Schlaggenwald. <sup>3</sup>	
	Rolled Tin. I. Per cent.	Bar Tin. II. Per cent.	Rolled Tin. III. Per cent.	Fine Tin. IV. Per cent.
Sn . . . . .	99·76	99·93	99·66	99·594
Cu . . . . .	—	—	0·16	0·406
Fe . . . . .	0·04	0·06	0·06	trace
As . . . . .	trace	trace	trace	trace

<sup>1</sup> *Elektro-metallurgie*, 1903, p. 465.

<sup>2</sup> Löwe, *Jahrb. der K. K. Berg-Academie*, vol. 13, pp. 63, 64.

<sup>3</sup> Löwe, *loc. cit.*

Banca tin is very pure, and on that account is not refined.

Banca Tin.		
	I.	II.
Sn . . . . .	99.961	99.99
Fe . . . . .	0.019	0.20
Pb . . . . .	0.014	—
Cu . . . . .	0.006	—

English Tin.			
	I.	II.	III.
Sn . . . . .	99.76	99.64	99.73
Fe . . . . .	trace	trace	0.13
Pb . . . . .	—	0.02	—
Cu . . . . .	0.24	1.16	trace

Tin from Pirlac in France. (Loire inférieure.)			
	I.	II.	III.
Sn . . . . .	99.5	97.0	95.0
Fe . . . . .	trace	2.8	1.2
Pb . . . . .	0.2	—	3.0

Tin from Pulo Braui.		Refined Tin from Pitkaranta.	
Sn . . . . .	99.76	Sn . . . . .	99.74
Sb . . . . .	0.07	Cu . . . . .	0.08
Pb . . . . .	0.02	Fe } . . . . .	0.18
Fe . . . . .	0.14	Pb } . . . . .	

The impurities in Banca tin from six different districts can be seen from the accompanying analyses<sup>1</sup>:—

	I.	II.	III.	IV.	V.	VI.
District.	Jobaes.	Blinju.	Sungei Liat.	Pankalpinang.	Merawang.	Sungei Stan.
Fe . . . .	0.0087	0.0175	0.0060	0.0060	0.0070	0.0196
Pb . . . .	—	trace	—	—	—	—
S . . . .	0.0099	0.0030	0.0040	0.0027	0.0090	0.0029
C . . . .	trace	trace	trace	trace	trace	trace

### *The Methods of Working up Refinery Dross*

The refuse from refining consists of: liquation dross, skimmings and scum from boiling.

The dross from the *Pauschen* process is added to the later slag charges.

In Cornwall the residue from liquating tin in a reverberatory furnace is remelted in a similar furnace and run into a small pot, where a difficultly fusible alloy containing tin separates out at the bottom. This alloy is subject to liquation at a higher temperature in a reverberatory furnace; in this way a portion of the tin is extracted, while hardhead remains in the furnace. This hardhead

<sup>1</sup> *Berg- und Hütten. Ztg.*, 1875, p. 454.

if it contain much arsenic, is not worked up any further; if free from arsenic it is added to charges of slag. The composition of the hardhead containing arsenic is:—

Fe . . . . .	62.50 per cent.
Sn . . . . .	17.25 „
As . . . . .	19.02 „
S . . . . .	1.26 „
<hr/>	
	100.03

At Banca the tin-iron alloy got by refining in pans is remelted in small shaft-furnaces and then liquated on iron plates. The residues from this process are thrown away. In other places liquation residues are added to ore- or slag-smelting charges, so that iron is slagged off with liberation of an equivalent amount of tin. Sometimes the liquation residues are submitted to repeated liquation, the end residues being rejected. No method has yet been devised for the treatment of these residues. Böhne<sup>1</sup> has suggested using them as anode material in the electrolysis of tin sulphate solutions. Other proposals have been made to convert them into lead-tin alloys, but these are not amenable to satisfactory treatment.

The scum from boiling, which consists of oxides of the foreign metals originally present in the ore, with a large proportion of tin oxide and metallic tin, is added to ore- or slag-smelting charges or is smelted with carbon in a reverberatory furnace. This yields tin and a black slag which contains prill, mechanically enclosed. The upper layers of tin collected in the tapping pot are sent into the market; while that in the lower portion of the pot is again liquated and boiled. The slag contains, besides prill, only about  $\frac{1}{2}$  per cent. of combined tin, and, after being stamped and the tin picked out, is thrown away.

#### I. C.—THE EXTRACTION OF TIN FROM SKIMMINGS AND OTHER BYE-PRODUCTS

Among these bye-products may be mentioned the drosses from melting tin, the so-called tin ashes, and the skimmings from the refining of crude lead which contains tin. Of other forms of refuse, tin plate cuttings may be quoted as a type.

*Dross produced in the fusion of tin* is added to the charges of ore

<sup>1</sup> Ger. Pat., No. 96198.

when smelted, or in the refining; should they be, however, in considerable quantity, they are sometimes smelted by themselves, in either shaft furnaces or reverberatory furnaces, the slag obtained being stamped and washed to extract the prill.

Before being treated in reverberatory furnaces, the drosses are formed into lumps, which are first liquated. The residue from this operation is sieved to separate the pulverulent portion, and then melted in a small reverberatory furnace on a sand-bed. The tin obtained in this way is known as *Aschen-zinn* (ash- or dross-tin). The slags are stamped and washed, the richer portions being smelted after the removal of prill by sieving.

Lead ores containing tin are worked at Freiberg. The tin collects with the silver in the lead, and is separated during cupellation, in the earlier less fusible scorïæ. These are worked up by a process devised by Plattner.<sup>1</sup>

The composition of the scorïæ which contain tin is as follows:—

PbO . . . . .	70·35 per cent.
SnO <sub>2</sub> . . . . .	12·53 „
Sb <sub>2</sub> O <sub>5</sub> . . . . .	12·50 „
As <sub>2</sub> O <sub>5</sub> . . . . .	4·73 „
CuO . . . . .	0·61 „
Ag . . . . .	0·25 „
	<hr/>
	100·97

These are first converted into work-lead, and litharge free from silver, by heating them in a reverberatory refining furnace with 5 per cent. of carbon as a reducing agent. The hearth of this furnace is 8 feet 3 inches long, 8 feet broad, and 1 foot 8 inches deep, and is trough-shaped, and in it 4 tons of scorïæ are treated in one day. The consumption of fuel for 100 parts by weight of scorïæ is 12½ parts of coal and 7½ parts of lignite; 100 parts by weight of scorïæ yield 46 parts of work-lead, containing 0·4 per cent. of silver and 53 parts of desilverised scorïæ. The average composition of the latter is:—

Pb . . . . .	58·0 per cent.
Sn . . . . .	11·5 „
Sb . . . . .	14·5 „
As . . . . .	7·0 „
Cu . . . . .	0·2 „
	<hr/>
	91·2

<sup>1</sup> *Jahrb. für das Berg- und Hüttenwesen in Sachsen*, 1883.

These desilverised scoriæ are "fined" (*frischen*) in shaft furnaces with one and a half times their own weight of slag consuming 25 per cent. of coke, and yielding tin-lead containing:—

Sn . . . . .	11·8 per cent.
Sb . . . . .	10·3     "
As . . . . .	3·5     "

This product, known as *Zinnfrischblei*, is converted by an oxidising roasting in a refining furnace into scoria which contains tin, and antimonial lead containing 15 per cent. antimony. The bed of this furnace is 5 feet 9 inches wide, 11 feet 6 inches long, and 14 inches deep, and the charges are each 2 tons in weight.

The scoria separated in this process, known as *erste Zinnpuder* ("first tin powder"), does not melt, and has a yellow colour, on account of the lead contained in it. Its composition is the following:—

Pb . . . . .	68·83 per cent.
Sn . . . . .	10·85     "
Sb . . . . .	11·89     "
As . . . . .	3·0     "
Cu . . . . .	0·56     "
	<hr/>
	95·13

3½ tons of this *Zinnfrischblei* are worked up in 24 hours, consuming 20 parts of coal and 15 parts of lignite per 100 of *Zinnfrischblei*.

The *erste Zinnpuder* is smelted in a shaft furnace with twice its weight of slag from the same process, or with slag from the first "fining" process. The coke used is 60 per cent. of the weight of *Zinnpuder*, and the product is called *second Zinnfrischblei*; each furnace smelts 7½ tons per day.

This *second Zinnfrischblei* is further converted into *antimonial lead* and *second Zinnpuder* by an oxidising roasting in a reverberatory furnace. These substances contain:—

Antimonial lead.		<i>Second Zinnpuder.</i>	
	Per cent.		Per cent.
Sb . . . . .	18·0	Pb . . . . .	44·74 to 49·86
As . . . . .	1·0	Sn . . . . .	27·59     "     24·28
Sn . . . . .	0·5	Sb . . . . .	13·22     "     11·97
		Cu . . . . .	0·95     "     0·48
		As . . . . .	2·72     "     0·95



The second *Zinnpuder* is smelted in a *Sumpf-ofen* in charges of 25 lbs. with 5 lbs. of coke, and yields tin-lead. This furnace is one with a deep receptacle at the bottom, in which the metal collects, below the tuyeres; it is 8 feet high and is provided with 2 tuyeres; it is 2 feet wide on the tuyere wall, 1 foot 4 inches wide on the front wall, and 1 foot 7 inches deep. The nozzles are 0·8 inch diameter, and the blast is worked under a pressure of 0·6 inch of mercury;  $1\frac{1}{2}$  tons of *Zinnpuder* are put through in the day. The tin-lead is remelted in a cast-iron pot, and, after the removal of the dross, contains:—

Sn . . . . .	33 per cent.
Sb . . . . .	14 „
As . . . . .	1 „

The slag obtained in the smelting of *Zinnpuder* contains considerable quantities of tin, both in a state of mechanical inclusion (up to 15 per cent.) and also in chemical combination. The following analysis gives its composition:—

SiO <sub>2</sub> . . . . .	28·65 per cent.
SnO <sub>2</sub> . . . . .	20·40 „
PbO . . . . .	5·81 „
CuO . . . . .	0·15 „
FeO . . . . .	26·61 „
MnO . . . . .	0·37 „
ZnO . . . . .	0·70 „
Al <sub>2</sub> O <sub>3</sub> . . . . .	12·00 „
CaO . . . . .	3·15 „
MgO . . . . .	0·79 „
S . . . . .	0·08 „
	<hr/>
	98·71

This is smelted in a shaft furnace by itself with 20 per cent. of coke, yielding the so-called *slag-tin-lead* and a slag which can be thrown away.

The former (the *slag-tin-lead*) contains:—

Sn . . . . .	32·6 per cent.
Sb . . . . .	14·6 „
As . . . . .	0·7 „

The composition of the latter is shown in the two following partial analyses :—

	I.	II.
SiO <sub>2</sub> . . . . .	29·82	30·8
SnO <sub>2</sub> . . . . .	5·3	8·8
PbO . . . . .	1·54	1·7
CuO . . . . .	0·18	—

The *slag-tin-lead* is melted in cast-iron pots, as the tin-lead is, and, like the latter, is an article of commerce.

### *Tin Cuttings*

Cuttings from tinned plate, which contain from 2 to 3 per cent. of tin (only exceptionally do they contain more), are worked up usually by wet methods, to extract the tin they contain. Dry methods have been proposed by Gutensohn, Laroque, and Edmunds.

Gutensohn's method consists in heating the cuttings with sand in revolving cylinders; the tin is melted off the iron, and takes the form of small grains; it is afterwards separated from the sand by sieving.

Laroque proposes to heat the cuttings with powdered charcoal and 0·5 per cent. of salt in a pot. This pot is fitted in the middle with a perforated diaphragm. The upper portion of the pot is heated to redness, while the portion below the diaphragm is cooled in water. The tin melts in the upper part of the pot, and falls through the diaphragm into the cooler region, where it collects.

Edmunds uses centrifugal machines, in the centre of which a fireplace is situated. The melted globules of tin are driven through the sieves of the apparatus and collect in the outer space of the machine.

Harpf<sup>1</sup> has proposed to utilise these cuttings for the preparation of tin-lead and tin-lead-antimony alloys in the extraction of lead. The method is to add the cuttings, either direct or after removing the tin, to the lead ores for smelting in shaft furnaces, the cuttings supplying the ferruginous material necessary for the process. If added direct the cuttings soon lose their tin owing to its low melting point, and the iron decomposes the lead sulphide at higher temperatures, liberating lead which alloys with the tin. If the lead is free from silver and if much copper be present, the alloy is liquated to get rid of the copper. The copper-free lead is then submitted to an oxidising

<sup>1</sup> *Oester. Zeitsch.*, 1897, Nos. 33 and 34.

refining process in a reverberatory furnace, whereby tin and antimony are oxidised and lead free from tin, along with tin-bearing scoræ, are produced. As tin is oxidised before antimony, the greater part of the latter goes into the second residue after the formation of the tin-bearing scoræ, and only a little mixes with the tin. If the lead be free from antimony, the tin drosses are worked up according to the method of Plattner described above; if it contains antimony, the first dross is treated in a shaft furnace for a tin-antimony-lead alloy, and the second dross containing most of the antimony is treated for hard lead. If the tin-bearing lead contains silver, then it may be pattinsonised or desilverised by the zinc process if the amount of tin be small; if considerable, it is liquated or refined before desilverising. In the former case, on refining after desilverising, the tin is obtained in the dross; in the latter case it is eliminated in the liquation dross before desilverising.

The cuttings are deprived of their tin before smelting with the lead ore in case too much tin is slagged off in the smelting process, or if, when the ores contain silver, the cost of refining before desilverising is too great owing to the large amount of tin present. The tin is removed either by the method of Edmunds described above, or by Patterson's method. This consists in dipping the tin-plate into a lead-bath, whereby the tin is dissolved and alloys with the lead. As the iron always retains some tin when Edmunds's process is adopted, it has been suggested to combine the two processes, obtaining, first, pure tin by Edmunds's method and then removing the remainder of the tin in the form of a tin-lead alloy.

These proposals of Harpf have not yet come into practice.

## II. THE EXTRACTION OF TIN IN THE WET WAY

Wet methods have been proposed to extract tin, and to prepare tin salts from tinned-sheet cuttings and from the waste water from dye works which contains tin. At present tin salts are obtained from tin cuttings in the wet way, and metallic tin from the same electrolytically.

*Extraction from Tin-plate Cuttings.*—A large number of methods have been proposed for this purpose; of these we shall only mention the most important.

Muir dissolves the tin from the cuttings in hydrochloric acid and precipitates it from the solution by means of zinc; steam is led into the solution during the precipitation. Milk of lime precipitates first the zinc and then the iron from the residual liquor.

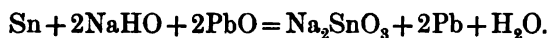


Schultze<sup>1</sup> treats the cuttings with acidified ferric chloride solution, and filters the resulting solution, which contains stannous and ferrous chlorides, through a mixture of stannous and ferrous oxides till it is saturated; after this the tin is precipitated by means of metallic iron. This is only possible if the solution be completely neutralised and contain stannous salts.

Moulin and Dolé's method consists in allowing gaseous hydrochloric acid to act on the cuttings until the iron is attacked. The resulting salts are dissolved out in water and the tin thrown down by zinc; the precipitate is washed with dilute sulphuric acid, dried, fused, and cast in moulds.

The so-called *argentín*, used in cloth-printing and in the manufacture of silver paper, is prepared by precipitating tin from an acidified solution of a tin salt by means of sheet-zinc. The tin-sponge which is obtained is washed and dried, and then ground to fine powder under water and passed through a sieve of hair or silk.<sup>2</sup>

Reineck'en-Pönsen and Kopp treat the cuttings in revolving barrels with soda lye, litharge, and steam; sodium stannate is formed with the separation of lead according to the following equation:—



The sodium stannate is either evaporated to dryness and sold as *preparing salt*, or the solution of it is precipitated by a stream of carbonic acid and the resulting oxide smelted with charcoal and chalk in a reverberatory furnace.<sup>3</sup> The spongy lead which separates out during the process is heated in a current of air, and converted into litharge, which is used over again.

It has also been proposed to treat the cuttings in revolving cylinders with quicksilver, and to separate the latter from the tin amalgam by distillation. Tin may be precipitated from the waste water of dye-works by granulated zinc or zinc powder, and the spongy mass dried and melted at a white heat with borax in order to volatilise the zinc.

Hunter, of Philadelphia, proposed to treat the cuttings with a warm solution of copper sulphate.<sup>4</sup> The tin is dissolved as sulphate and metallic copper is deposited. When the tin is all dissolved and

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1894, p. 208.

<sup>2</sup> Mullerus, *Chemiker-Zeit.*, 1891, No. 64.

<sup>3</sup> *Der Maschinenbauer*, 1879, p. 80.

<sup>4</sup> German Patent, class 40, No. 78,344, January 3rd, 1894.

the iron is exposed, the latter precipitates the tin from solution, and is dissolved with the formation of ferrous sulphate. The deposit of copper and tin thus obtained is melted up together, forming an alloy, or it is treated by well-known methods to separate the metals.

Most of these methods have probably fallen into disuse, as tin is at present prepared electrolytically on a large scale.

Many proposals have also been made for the preparation of salts of tin from tinned-plate cuttings.

Tin chloride is prepared at Uetikon, on the Lake of Zurich,<sup>1</sup> by treating the cuttings with dry chlorine gas. The process is conducted in a fixed iron cylinder 13 feet high and 3 feet 3 inches diameter, fitted with a perforated false bottom, on which the cuttings are placed, the chlorine being introduced below it. The tin is converted into stannic chloride, which collects as a fuming liquid in a receiver under the cylinder. By cautious addition of water *solid tin chloride* is precipitated, which is sold in that form, and is used in dyeing.

Donath's process is one in which the cuttings are boiled with concentrated soda lye and pyrolusite; the solution of sodium stannate which is obtained is treated with acetic acid to precipitate stannic acid.

Scheurer-Kestner prepares sodium stannate by moistening the cuttings in a current of air with soda lye of 18° to 20° B.

Carez's method is to act on the cuttings with a solution of alkaline polysulphides containing salammoniac. The solution is from 30° to 50° or 60° B. in strength. Any lead which may be present is separated as lead sulphide and the tin is dissolved, being afterwards precipitated by hydrochloric acid as sulphide of tin.

Lambotte proposes to expose the cuttings at a temperature of 100° C. to a stream of chlorine and air, and condense the escaping vapour of stannic chloride, or to lead it into a dilute solution of tin chloride.

Kunzel<sup>2</sup> treats the cuttings with hydrochloric acid or nitric acid, precipitates the tin from the solution by zinc, dissolves the resulting spongy tin in hydrochloric acid, and allows the stannous chloride to crystallise. The residual liquors are worked up for the production of green vitriol or iron.

<sup>1</sup> Lunge, *Bericht über die Chem. Indust. auf der Schweizer Landes-Ausstellung in Zurich*, 1883. Zurich, 1884, p. 29.

<sup>2</sup> *Berg- und Hüttenm. Ztg.*, 1874, p. 57.

*The Purification of Tin in the Wet Way*

This is very costly and is only used in exceptional cases, as, for instance, when it is desired to prepare tin compounds from pure tin. It consists in dissolving granulated tin in hydrochloric acid; so long as the tin is in excess, the impurities remain for the most part in the undissolved portions. The tin is precipitated from the solution by zinc, and the spongy deposit washed with dilute acid and with water.

## III. THE EXTRACTION OF TIN BY ELECTROLYTIC METHODS

The proposals which have hitherto been made, for the application of electro-metallurgical methods to ores and slags, do not seem to have much chance of success; but those for the treatment of tinned plate cuttings, and for refining tin, by these methods, appear to be more likely to succeed.

*Treatment of Ores.*—For this, Burghardt,<sup>1</sup> and Vortmann and Spitzer,<sup>2</sup> have proposed methods. Burghardt proposes to fuse the finely divided ore with excess of caustic soda, to extract the sodium stannate from the fused mass with water, and to separate the tin from the solution by electrolysis. Sheet-iron is used for the anodes, and plates of tin, iron, or some other metal for the cathodes. The temperature of the solution for electrolysis should be 60° C. If arsenic, antimony, or sulphur be present in the ores, they should be removed by roasting before the ore is fused with caustic soda. According to Borchers<sup>3</sup> the current is soon interrupted by the deposition of oxides of tin on the anode plates; he states that it is impossible to extract tin with profit in this way.

Vortmann and Spitzer's method consists in converting the tin of the ores or drosses, previously freed from sulphides, into sodium sulphostannate, by fusing them with three times their weight of a mixture of 2 parts of soda-ash to 1 of sulphur. The solution of sulphostannate, after the addition of ammonium compounds, is electrolysed between anodes of lead and cathodes of tinned sheet-copper. Borchers<sup>4</sup> points out that there is no material which can stand the production of sulphostannate by a process of smelting; even in a reverberatory furnace its production is said to be possible only with great loss of tin and high cost for repairs. This method has not found any practical application.

<sup>1</sup> German Patent, No. 49,682, July 1st, 1889.    <sup>2</sup> *Ibid.*, No. 73,826, Sept. 14th, 1893.

<sup>3</sup> *Elektro-metallurgie*, p. 154.

<sup>4</sup> *Loc. cit.*, p. 301.

Shears<sup>1</sup> has proposed the following method for the recovery of tin from slags. The slags are first fused with alkalis and the alkaline stannate lixiviated out with water. The tin is precipitated from the solution by the electric current in the way described above. Silica and alumina are precipitated from the residual liquor by milk of lime and are used for the manufacture of cement; the alkali is recovered in the usual way.

If wolfram is present, it is found in the last liquors, and can by evaporation be separated as tungsten salts. This method has also found no application.

Bohne<sup>2</sup> proposes granulating the slags and treating them with hot dilute sulphuric acid, whereby a solution of sulphates of tin and iron is obtained, along with a residue partly consisting of gelatinous and partly of granular silica containing 0.5 to 0.8 per cent. of tin. The tin is then to be precipitated electrolytically from the solution, using anodes of granulated hardhead. The siliceous residue, after drying and mixing with 2 to 3 parts of quartz sand, may be used for making furnace beds for the smelting of tin ores. The acid treatment of the granulated slag takes place in lead-lined wooden boxes, the temperature being soon brought up to the point required (60° to 70° C.) by the use of a Körting stirrer. After saturation the liquor is diluted, filtered through a press, and then electrolysed. This process was employed for some time at Tostedt, but has been given up.

Brandenburg and Weyland<sup>3</sup> heat up the powdered slag with bisulphate solution to dissolve the tin, the silica separating out as a jelly. The solution is then electrolysed. Nothing is known as to the application of this process.

Many methods have been suggested for the recovery of tin from tin-plate cuttings by means of the electric current, as, for instance, those of Keith, Gutensohn, Walbridge, Beatson, Price-Fenwick, Morin, Minet, Smith, and Vortmann and Spitzer. Meyer, Quintaine, Coleman and Cruikshank. These for the most part, however, do not appear to have come into use. Both basic and acid electrolytes have been suggested, but only the former have come into continuous use.

Borchers<sup>4</sup> has proposed to use for this purpose as an electrolyte, a 12 to 15 per cent. solution of common salt, containing 3 to 5 per cent. of sodium stannate. In consequence of the high conducting power of salt solution, this electrolyte serves much better than pure sodium stannate for the purpose. With a current of 50 to 150

<sup>1</sup> English Patent, No. 9,821, June 14th, 1889.

<sup>2</sup> German Patent, No. 96,198.

<sup>3</sup> *Ibid.*, No. 123,764.

<sup>4</sup> *Loc. cit.*, p. 154.

ampères per square metre and a potential of 2 to 3 volts, he obtained from cuttings (free from solder) a spongy metallic precipitate, the temperature of the bath being from 40° to 50° C.; the precipitate, after washing and drying, could be melted and cast. The bath must be kept distinctly alkaline; as the quantity of tin oxide in the bath increases, alkali must be added. Towards the end of the process the solution becomes so concentrated that it is more profitable to work it up for *preparing salt*, by evaporating it to dryness, than to continue the electrolysis. The advantages of this process are stated by Borchers<sup>1</sup> to be, the possibility of completely removing the tin from the cuttings, the production of a residue of clean sheet-iron, the possibility of producing a tin quite free from iron, the practicability of using an iron vessel which itself forms the cathode, and the use of an iron basket as anode. This process has only been tried in a small way.

Keith uses as electrolyte a solution of caustic soda and sea-salt. The mixture is placed in an iron pan, and the cuttings, which are connected with the positive pole, are hung in the electrolyte in a basket. The wall of the vessel serves for a cathode.

Beatson<sup>2</sup> uses a hot solution of soda, to which potassium cyanide has been added. Iron plates are used as the anode, or the wall of the vessel, if it is made of iron, serves the purpose. It must be pointed out that a solution of potassium cyanide is rapidly decomposed when kept at the boiling point.

According to a newer patent<sup>3</sup> the inventor uses a solution of alkaline hydrate as electrolyte, and the deposit of tin obtained is electrolytically purified in a solution of tin chloride; in order to obtain the tin in a compact form it is deposited on revolving rolls.

Price<sup>4</sup> uses soda lye as electrolyte; there are others who do the same.

Walbridge makes use of a solution of caustic soda and sodium nitrate for the purpose.

Vortmann and Spitzer proposed that their above-mentioned method for the extraction of tin from ores should also be applied to the recovery of tin from cuttings. The conversion of tin into sodium sulphostannate was to be effected by heating the cuttings with half their weight of a mixture of sulphur and soda-ash.

*Sulphide of Tin*, which is a bye-product in the preparation of some organic colouring matters, can be converted into sodium sulphostannate by boiling it with a solution of sodium polysulphides.

<sup>1</sup> *Loc. cit.*, p. 396.

<sup>2</sup> English Patent, No. 11,067, Sept. 18th, 1885.

<sup>3</sup> *Ibid.*, No. 12,200, 1892.

<sup>4</sup> *Ibid.*, No. 2,119, 1884.

As acid electrolytes, sulphuric acid and acid sulphates and chlorides have been proposed by Gutensohn,<sup>1</sup> and Fenwick.<sup>2</sup>

Changy makes use of a solution of stannous chloride to which ammonium chloride or hydrochloric acid has been added.

Raymond's proposal is to adopt a solution of stannous chloride at 5° to 6° B. acidified with hydrochloric acid, and to lead the current into the bath through iron rods.<sup>3</sup> Meyer<sup>4</sup> electrolyses at high current densities in dilute hydrochloric acid. Quintaine<sup>5</sup> proposes to use acid tin sulphate solution. It has also been proposed to treat the tin clippings outside of the electrolytic bath with ferric or stannic chloride, and to electrolyse the solution of ferrous and stannous chloride thus produced, using anodes of carbon. The tin would thus be deposited and the solution regenerated.

The following method, invented by Smith, is said by F. Fischer<sup>6</sup> to have been tried in Berlin and in England. Dilute sulphuric acid is the electrolyte, and tinned copper plates are used as the cathode. The tin cuttings themselves form the anode: they contain from 3 to 9 per cent. of tin and are suspended in a wooden cage in the liquid. The vats are lined on the inside with caoutchouc. The cuttings are bound together with long strips of tinned iron, and by the copper wire which carries the current. The dynamo gives a 240 ampère current with an electromotive force of 15 volts, and absorbs 7 horse-power. The baths are 8 in number and are 5 feet by 2 feet 4 inches by 3 feet 3 inches in size. Each set of four is formed by placing divisions in a wooden vat 10 feet by 5 feet. The cathodes, 4 feet by 3 feet by 0.06 inch, are suspended vertically in front of the anodes at distances 4 inches apart.

The electrolyte is made by diluting 1 part by measure of sulphuric acid at 60° B. with 9 parts of water.

The tin separates in the form of a sponge as long as the solution is acid, but as the bath becomes more and more neutral the deposit becomes pulverulent and even crystalline; it is purer than ordinary commercial tin and dissolves more rapidly than the granulated metal in acids; it is therefore used for the preparation of tin salts. As soon as the tin is removed from the surface of the iron, the latter is attacked and collects in such quantities in the electrolyte that the latter must be renewed every seven weeks; it is worked up for the manufacture of green vitriol.

<sup>1</sup> German Patent, No. 12,883.

<sup>2</sup> English Patent, No. 8,988, of 1886.

<sup>3</sup> *Electrotech. Zeitschr.*, 1892, p. 573.

<sup>4</sup> U.S.A. Patent, No. 660,116.

<sup>5</sup> German Patent, No. 118,358.

<sup>6</sup> Wagner-Fischer's *Jahresberichte*, 1885, p. 173.

According to theory, 240 ampères in 8 baths should yield per hour 9·37 lbs. of tin; actual working, however, produces only the half of this amount. The principal reason for this proportionally small output is that the current dissolves iron as well as tin as soon as the former is exposed.

Electrolysis in basic baths has succeeded on a large scale, *e.g.*, at Goldschmidt's works in Essen, where 13,000 tons of tin cuttings are treated yearly, at H. W. von Linde's works in Crefeld, at the works of the Vulcan Detinning Co. in Sewaren, N.J.; of the Ammonia Co. at Philadelphia, and of Johnston and Jennings Co. at Cleveland and Chicago.

According to Mennicke<sup>1</sup> the anodes consist of the tin clippings loosely packed in wire baskets, the cathodes of sheet-iron, or the iron bath itself, the electrolyte of caustic soda containing 6 to 7 per cent. of  $\text{Na}_2\text{O}$ . This strength of caustic must be preserved during the course of the electrolysis. The electrolyte has to be frequently replaced since it changes greatly in composition during the process, through solution of tin, absorption of carbon dioxide from the air, and precipitation of stannic acid by the carbon dioxide thus absorbed. The alkaline bath contains on an average 3 to 5 per cent. of caustic reckoned as  $\text{Na}_2\text{O}$ ; 1 to 1·5 per cent. of  $\text{Na}_2\text{O}$  is in combination with 3 per cent. of  $\text{SnO}_2$  (or 2·34 per cent. of Sn) in the form of sodium stannate, and 1·7 to 2·8 per cent. of  $\text{Na}_2\text{O}$  is combined with carbon dioxide as sodium carbonate. The electrolyte becomes gradually more concentrated during the process with compounds of lead and iron, and with soap, which arises from the saponification of the resin, varnish, and fat clinging to the scrap metal. If the electrolyte does not contain chlorides, then but little iron and lead is taken up.

The liquor is regenerated by being treated hot with carbon dioxide, which, according to Mennicke, precipitates the iron and lead as carbonates and the tin as stannic acid; the caustic is converted into carbonate at the same time, and caustic soda is regenerated from this by the action of lime. Soap is removed by cooling the liquor down to  $-5^\circ\text{C}$ .

The baths are connected directly with the negative leads, and the positive leads are brought in contact with copper bars or tubes, isolated on the longer sides of the bath. This copper is put in metallic connection with the iron strips wrapped round the baskets,

<sup>1</sup> *Zeit. für Elektrochemie*, 1902, pp. 315, 357, 381. *Sammlung chem. tech. Vorträge von Ahrens*, vol. vii. (Wiedergewinnung des Zinns von Weissblechabfällen), Stuttgart, 1902. Borchers, *Elektro-metallurgie*, 1903, p. 460.

which themselves are made of an open network of iron wire. The baskets are shaped to fit into the baths, and are of such size that they can be readily moved in and out of them. If the baths hold 100 cubic feet, then the baskets contain 100 lbs. of cuttings, the ratio in volumes of basket to bath being about 3:5. This suffices to prevent short-circuiting and at the same time to bring down the resistance of the electrolyte to the lowest point. The baskets are hung side by side in the bath. The cathode area may be increased by arranging sheets of iron between the baskets, but in that case the baskets must be set somewhat apart in order to prevent short-circuiting. As the cuttings must be loosely packed to allow of the free passage of the electrolyte to all parts, it is necessary to loosen them often during the course of the operation with iron hooks.

The electrolyte is warmed in high-standing tanks by fires or steam to  $90^{\circ}$ , so that it has the right temperature ( $60^{\circ}$  to  $70^{\circ}$  C.) for carrying out the electrolysis. The liquor is led from these tanks into a main pipe, and thence by separate pipes into the baths. It flows from these through outlet pipes into a main channel and then into a collecting pot, from which it is raised into the supply tanks. The outlet pipe is fitted with a sieve and overflow, so that fragments of tin are held back.

During the circulation of the electrolyte there is considerable evaporation, and this must be made good by the addition of hot water (from the condensers). According to Mennicke there are 7,000 cubic feet of liquor in circulation in a plant of 50 baths, each of 100 cubic feet capacity, and the loss from evaporation is 350 cubic feet per 24 hours.

The average tension of the baths is 1.5 volts, though, owing to the uneven character of the anode surfaces, the strength and tension of the current are constantly varying. The time taken to deprive the cuttings entirely of tin is from 5 to 7 hours when the average tension is 1.5 volts and when the temperature and composition of the electrolyte are kept fairly constant and the cuttings are similar in character. In a year of 300 working days 9,000 tons of scrap can be worked off in a plant consisting of 60 baths each of 100 cubic feet capacity, 50 of these baths each with 3 baskets holding 110 lbs. of cuttings being in constant operation.

The tin produced is spongy. If sufficiently pure it is washed, pressed, thoroughly dried, and melted down in a tin bath; if impure it is treated in a shaft or reverberatory furnace. The iron after removal of the tin is sold for treatment in the Siemens-Martin furnace. Arrangements for charging and withdrawing the



cuttings during the operation have been proposed by Matthews and Davies<sup>1</sup> and by Coleman and Cruikshank.<sup>2</sup> Becker<sup>3</sup> proposes packing the cuttings in a perforated wooden box of rectangular horizontal section, the sides of the box being made to lift up. Metallic connection is set up through pointed vertical rods embedded in the cuttings, and metal rods attached to these and resting on top of the boxes. It may be noted, however, that wood is attacked by caustic soda.

*The Refining of Tin by Electro-metallurgical Methods.*—A. Brand<sup>4</sup> has carried out experiments on the refining of tin by the electric current, but this method does not seem to have found practical application. These experiments showed that the tension in a bath with tin anodes and a solution of stannous chloride containing 5,040 grains per gallon and 2.5 per cent. by volume of concentrated hydrochloric acid, amounted to 0.058 volt (14.8 ampères); with 7.5 per cent. of hydrochloric acid it was only 0.031 volt.

A current of 1 ampère deposits 2.195 grams of tin per hour: 455.6 ampères are therefore necessary for the deposition of 1 kilo. per hour. The energy required for the extraction of 1 kilo. of tin per hour may be calculated as:—

$$0.058 \times 455.6 = 26.424 \text{ Watts;}$$

or

$$\frac{26.424}{75 \times 9.81} = \frac{26.424}{735} \text{ H.-P.}$$

The loss of energy, in the conversion of mechanical into electrical energy, may be taken as 12 per cent. Further, the loss due to conversion of electric energy into heat, short-circuiting, &c., may be taken as 25 per cent., so that the actual consumption of energy may be reckoned at

$$\frac{0.058 \times 455.6}{735 \times 0.88 \times 0.75} = 0.054 \text{ H.-P.}$$

Assuming that one horse-power per hour requires 2 kilos. of coal, the coal required for the extraction of 1 kilo. of tin would be 0.11 kilo. As the principal impurity of tin, viz., iron, collects in the electrolyte and is not separated from it, fresh quantities of electrical energy will be continually introduced into the circuit.

Claus<sup>5</sup> has proposed a method for refining tin, which according to

<sup>1</sup> English Patent, 1900, No. 21,533.

<sup>2</sup> German Patent, No. 119,986.

<sup>3</sup> German Patent, No. 118,249; English Patent, 1900, No. 3,524.

<sup>4</sup> Dammer, *Chem. Tech.*, vol. ii., pp. 27, 28, 324.

<sup>5</sup> *Elektrochem. Zeitschr.*, viii., pp. 168, 169.

Cowper Coles has been used on a practical scale. The electrolyte consists of sodium sulphostannate, and the anodes of the tin to be refined. The impurities, all but antimony and arsenic, collect in the anode slimes or (as in the case of gold, silver, zinc, lead, copper, and iron) are precipitated as sulphides. Antimony and arsenic, if present, are precipitated on the cathode along with the tin. In this case, the cathode deposits are used as anodes in a bath containing a solution of sodium thiosulphate in hydrochloric acid; this effects the removal of the antimony and arsenic as insoluble sulphides. The best results have been obtained by using a solution of sodium sulphostannate heated up to  $90^{\circ}\text{C}$ ., the specific gravity of the solution being 1.07 and the current density 90 ampères per square yard.

In some cases Claus uses a solution of sodium sulphide, or of caustic soda or potash, as electrolyte. Sodium sulphostannate solution can be prepared by melting impure tin with the equivalent amount of sulphur and soda, or with sodium sulphate and carbon; the melt is dissolved out with water. The difficulties in the preparation of this compound have already been described.

## ANTIMONY

### PHYSICAL PROPERTIES

ANTIMONY is characterised by its great brilliancy and by its colour, silver white with a slight tinge of blue; the latter is increased by the presence of impurities in the metal. When deposited from a solution by zinc it takes the form of a black powder. When melted antimony is allowed to cool slowly, it exhibits a coarsely foliated structure; rapid cooling makes it granular and crystalline. Antimony crystallises, like the isomorphous metals bismuth, arsenic, and tellurium, in the forms of the hexagonal system. Its specific gravity has been determined to lie between 6.6 and 6.8. Schröder has given it as 6.697 compared with water at 4° C.

Antimony is brittle and can easily be powdered in a mortar. It is harder than copper. Its coefficient of linear expansion by heat between 0° and 100° C. is, according to Calvert and Johnson, 0.000985. It melts between 440° and 450° C. (Pictet). In passing from the liquid to the solid state it does not expand as bismuth does. Carnelly and Carleton-Williams state that its boiling point is between 1090° and 1450° C. According to Demarcay it boils in a vacuum at the temperature of 292° C. It burns in the air forming oxides, but can be distilled in a stream of hydrogen.

When pure molten antimony is allowed to solidify slowly and without disturbance under a layer of slag, a fern-like appearance; of raised lines radiating from the centre, appear on the solidified surface of the metal. This is the so-called "antimony star" or "regulus antimonii stellatus." On small castings there will be only one such star in the middle of the surface, but larger castings will show many intersecting ones.

This appearance is not produced in impure antimony nor in the pure metal unless it is kept very still and covered during cooling by a layer of slag. As it is generally regarded as an indication of the

purity of the metal, pure antimony, which does not possess it, is always re-melted and cooled under the required conditions. If molten antimony be allowed to fall upon a sheet of paper, it is broken up into numerous small drops which burn with great brilliancy.

Its specific heat, as determined by Regnault between  $0^{\circ}$  and  $100^{\circ}$  C., is 0.0508. Its conductivity for heat, compared with that of silver as 1000, was determined by Calvert and Johnson: along its axis of crystallisation it is 215, and at right angles to this direction it is 192. Its electrical conductivity, compared with that of silver as 100, is 4.29 at  $18.7^{\circ}$  C., according to Matthiessen.

Commercial antimony is generally contaminated by small quantities of sulphur, arsenic, lead, copper, and iron. These cause the above-mentioned blue tinge in its colour.

#### PROPERTIES OF ANTIMONY AND OF ITS COMPOUNDS WHICH ARE OF IMPORTANCE FOR ITS EXTRACTION

Antimony is not affected by exposure to air at ordinary temperatures, but at temperatures above its melting point it oxidises rapidly. Metal which has been reduced from the oxides by charcoal in presence of alkalis frequently tarnishes in the air. The cause of this is said to be a small quantity of alkali which is retained by the metal and absorbs moisture with liberation of hydrogen.

When antimony, which has been raised to a red heat, is allowed to fall from a sufficient height on to a plate, it is dissipated in a mass of brilliant sparks, forming a dense white cloud of oxide.

Antimony is attacked by hydrochloric acid only when it is in the state of very fine powder: hydrogen is then liberated. Sulphuric acid does not attack it, when dilute: the hot concentrated acid, however, forms with it antimonious sulphate, sulphur dioxide being at the same time liberated. Nitric acid attacks antimony, producing, according to its temperature and degree of concentration, a mixture of the trioxide and tetroxide of the metal in different proportions. These oxides are insoluble in the acid.

Aqua regia in the cold dissolves antimony easily, forming the penta-chloride.

In a current of steam, at a red-heat, antimony is slowly converted into oxide.

When ignited with nitre and soda it explodes, forming an alkaline antimoniate: with a smaller proportion of nitre it also forms some trioxide.

The metalloids, with the exception of boron, carbon, and silicon, all form compounds with antimony.

*Antimony Hydride, SbH<sub>3</sub>*

Antimony forms only one compound with hydrogen, antimonuretted hydrogen. This is a colourless, inflammable gas, which burns with a greenish flame producing a white smoke of steam and antimony trioxide. It is formed when hydrogen is generated in the presence of a soluble antimony compound, or when alloys of antimony with the alkali metals are decomposed by water, or when an antimony-zinc alloy is treated with sulphuric or hydrochloric acid. When this gas is led through a heated glass tube, antimony is deposited in the cold part of the tube in the form of a mirror. If a mixture of this gas with hydrogen be passed through a solution of silver nitrate, a black precipitate of silver antimonide,  $\text{SbAg}_3$ , and silver is deposited.

## OXIDES OF ANTIMONY

Antimony forms three oxides: Antimony trioxide,  $\text{Sb}_2\text{O}_3$ , Antimony tetroxide,  $\text{Sb}_2\text{O}_4$ , and Antimony pentoxide,  $\text{Sb}_2\text{O}_5$ . The pentoxide forms two acid hydrates—Antimonic acid,  $\text{HSbO}_3 + 2\text{H}_2\text{O}$ , and metantimonic acid,  $\text{H}_4\text{Sb}_2\text{O}_7$ .

*Antimony Trioxide or Antimonious Oxide, Sb<sub>2</sub>O<sub>3</sub>,*

is formed by heating antimony or sulphide of antimony in the air; it is a white powder which becomes yellow when heated, regaining its whiteness on cooling. It melts at a dark red heat forming a yellow liquid which solidifies to a grey mass resembling asbestos. It is volatile, and can be sublimed. If heated in the air it is converted into the tetroxide, which is not volatile. If the vaporised trioxide and air be passed over ignited, finely divided oxides of those metals which form compounds with antimonic acid, the latter is formed and combines with the oxides producing antimoniates.

It is insoluble in water, sulphuric acid, or nitric acid, but is easily dissolved by hydrochloric and tartaric acid and by caustic alkalies. With antimony sulphide it melts without decomposition, forming the so-called antimony-glass. The trioxide is poisonous, especially in the form of vapour.

*Antimony Tetroxide or Antimonic Antimoniate, Sb<sub>2</sub>O<sub>4</sub>,*

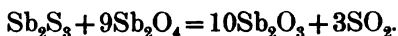
is a white powder which is neither fusible nor volatile. It can be prepared by heating the trioxide in the air or by igniting the pentoxide. Hydrochloric acid dissolves it readily. It is a metallurgical product, being known under the name of "antimony ash" or

"cinis antimonii," but in this form always contains some trioxide. If the antimony ash be ignited with charcoal and alkaline carbonates, metallic antimony is obtained; if the alkali be omitted, the greater portion of the antimony will be volatilised as trioxide, a small part only being obtained in the metallic state.

If the tetroxide be fused with metallic antimony in the proper proportion, the trioxide is formed:—



When the tetroxide is fused with antimony sulphide in suitable proportions, sulphur dioxide is liberated, and the trioxide is formed, which, however, always retains more or less of the sulphide:—



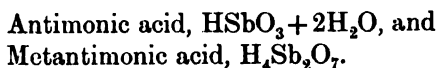
This impure trioxide of antimony, the colour of which varies with the quantity of sulphide it contains, is known as "antimony-glass," and is used as a colouring matter in glass making, more especially in the preparation of artificial gems.

*Antimony Pentoxide or Antimonic Anhydride,  $\text{Sb}_2\text{O}_5$ .*

This is a bright yellow powder and can be prepared by treating antimony with nitric acid. The powder obtained must be repeatedly evaporated to dryness with nitric acid to completely oxidise the tri- and tetroxides which are at first formed, and the residue gently ignited.

The pentoxide is insoluble in water and in nitric acid, but dissolves slowly in concentrated hydrochloric acid; it is converted on ignition into the tetroxide.

Antimonic anhydride forms two hydrates, each of which forms a series of salts, viz. :—



Antimonic acid is used to replace arsenic acid in the manufacture of aniline yellow and aniline red.

CHLORIDES OF ANTIMONY.

Antimony forms two compounds with chlorine, viz. :—

Antimonious chloride or antimony trichloride,  $\text{SbCl}_3$ , and  
Antimonic chloride or antimony pentachloride,  $\text{SbCl}_5$ .

The trichloride is formed when antimony trisulphide is boiled with concentrated hydrochloric acid; also when the metal or the trisulphide is heated with corrosive sublimate. It is soluble in hydrochloric acid, is volatile, and can easily be distilled. When the solution of it in hydrochloric acid is diluted with water, white basic chloride of antimony is precipitated: this is known as "powder of Algaroth," and was formerly used in medicine.

The pentachloride is formed with evolution of light when chlorine acts on antimony. According to Gore, antimony in the form of a grey amorphous mass is deposited when a strongly acid solution of the pentachloride is electrolysed. This contains, in addition to small quantities of free hydrochloric acid, from 3 to 20 per cent. of antimony pentachloride, and explodes if heated to 200° C.

#### SULPHIDES OF ANTIMONY.

There are two compounds of sulphur and antimony, viz. :—

Antimony trisulphide,  $\text{Sb}_2\text{S}_3$ , and

Antimony pentasulphide,  $\text{Sb}_2\text{S}_5$ .

The trisulphide is known in both the crystalline and the amorphous condition. The crystalline form is found in nature as antimony glance or stibnite; it possesses a greyish black colour, metallic lustre and crystalline structure. It can be melted, out of contact with the air, at a red heat, and volatilises without decomposition at a strong white heat.

The amorphous trisulphide can be prepared artificially, and possesses, according to the method of its preparation, a red or orange colour.

The red trisulphide, which formerly was used in medicine under the name of "Kermes mineral," can be prepared by boiling antimony glance with carbonate of potash or soda. The antimony sulphide is deposited from the solution on cooling as a reddish-brown powder. It always contains variable quantities of antimony trioxide and alkali.

The orange-coloured trisulphide can be obtained by precipitating solution of an antimonious salt with sulphuretted hydrogen: this precipitate always contains water. The so-called *antimony cinnabar* is a red amorphous trisulphide containing the trioxide; it is prepared by treating a solution of antimony in hydrochloric acid with thiosulphate of calcium or thiosulphate of sodium. It is used as a pigment in oil painting, on account of its fiery red colour.

When antimony sulphide is calcined in a current of air, antimony trioxide and sulphur dioxide are formed, the former being partly

volatilised, and partly converted into the tetroxide; the sulphate is not formed. The trisulphide is easily fused, and therefore the roasting of it is difficult.

When a mixture of air and steam is passed over the trisulphide the trioxide is formed with liberation of sulphuretted hydrogen; in this case also the sulphate does not appear to be produced. Antimony is reduced from the trisulphide at a red heat by the action of hydrogen, hydrocarbons, iron, and zinc. According to Karsten, charcoal has the same effect, but only at a temperature above the boiling point of the metal.

The trisulphide is soluble in hot concentrated hydrochloric acid, forming antimony trichloride. If it be treated with a solution of a caustic alkali or an alkaline carbonate, or of an alkaline sulphide, or if it be fused with these bodies in the solid state, substances called *sulphantimonites* are produced, *e.g.*



These *sulphantimonites* are soluble in water when they contain a large proportion of basic sulphides, but a large proportion of antimony renders them insoluble. The trisulphide and the trioxide do not mutually decompose each other as is the case with galena and litharge, but fuse together undecomposed to form the so-called *antimony-glass*.

When the trisulphide is fused with the penta- or tetroxide, sulphur dioxide and the trioxide are formed: the latter takes up some of the undecomposed trisulphide and forms with it *antimony-glass*.

The pentasulphide of antimony,  $\text{Sb}_2\text{S}_5$ , is an orange-coloured powder, known in medicine as *golden sulphide of antimony*. It can be obtained by the action of sulphuric acid on the so-called sulphantimoniates. These latter substances are prepared by boiling antimony glance with a solution of an alkaline polysulphide, or by fusing the two substances together in the solid state. *Schlippe's salt*,  $\text{Na}_3\text{SbS}_4 + 9\text{H}_2\text{O}$ , is one of these sulphantimoniates.

The pentasulphide, when heated in the absence of air, yields the trisulphide, sulphur being separated.

Hydrochloric acid converts it into the trichloride with separation of sulphur. In other respects the pentasulphide behaves like the trisulphide. It is used principally, at the present time, as a red pigment and for vulcanising india-rubber.

#### OXY-SALTS OF ANTIMONY.

The most important of these is *tartar emetic* or potassium stibnate,  $\text{C}_4\text{H}_4\text{K}(\text{SbO})\text{O}_6$ , used in medicine.



## ALLOYS OF ANTIMONY.

Antimony alloys with most metals, making them brittle. It is added to lead to harden it. When alloyed with tin it renders it silvery in appearance, increases its hardness, and raises its melting point. The alloys of tin and antimony have been exhaustively studied by Staed.

The most important alloys of antimony are *type-metal*, which consists of lead, tin, and antimony, or of only lead and antimony; *hard-lead*, produced by working lead ores which contain antimony, and which consists of lead and antimony in very varying proportions; *britannia-metal* and *white-, bearing-, or antifriction-metal*, which consist principally of antimony and tin, with addition of lead, copper, zinc, bismuth, and nickel. *Britannia-metal*, which is used for the manufacture of teapots, spoons, plates, &c., contains, according to Ledebur, tin 85 to 93 per cent., antimony up to 10 per cent., and copper up to 3 per cent. English *plate pewter* and *queen's-metal* are similar alloys.

## ANTIMONY ORES.

*Antimony Glance, Sb<sub>2</sub>S<sub>3</sub>.*

Antimony glance is the most important ore of antimony: it is also known by the following names—*grey antimony ore*—*antimonite*—*stibnite*. It contains 71·77 per cent. of antimony and 28·23 per cent. of sulphur. It occurs in long rod-like or needle-like rhombic crystals, or in the massive state, or disseminated in fibrous or compact particles. It frequently contains gold and silver, and usually arsenic also; its more commonly associated minerals are quartz, calc-spar, heavy-spar, and spathic iron ore; zinc blende and galena frequently occur intimately mixed with it.

It occurs in Germany (Arnsberg, Erzgebirge, Fichtelgebirge, the Harz), in Bohemia (Milleschau, Hatc, Brodkowic, Przibram, Schönberg, Michaelsberg), in Hungary (Kremnitz, the Rechnitz Hills, Toplitzka, Schemnitz, Felsöbanya, Nagybanya, Dobschau, Rosenau, Gisno, Gross-Jöllnitz, Magurka), in Servia (Losnica, Kostajnik), in Bosnia, Serajewo), in France (Auvergne, Gard, Ardèche, Aude, Vendée, Lyonnais, Haute Loire, Bouc, Septèmes near Marseilles, and the Cantal, Corsica), in Italy (Tuscany and Sardinia), in England (Cornwall), in Spain (Estremadura and Badajoz, Caurel, Brollon, Orense), in Portugal (Oporto and Braganza), in Algiers (Province of Constantine), in Canada (Rawdon, Nova Scotia), in California (Havilah, Bousby, Erskine Creek, Grace Darling, Padre, San Emidio in Kern County,

Crowell in Riverside County<sup>1</sup>), Nevada, Arkansas (Sevier County), Utah (Garfield County), Idaho (Kingston), South Dakota, Mexico, Nicaragua, Chili, Peru, Turkey (Adrianopolis Monastyr, Rozdan, Mytilene, Chios, Aidin, Endemisch); in Asia it occurs in Borneo, India, Tenasserim, Shigri, Jhelum District<sup>2</sup>), China (Nanning, Ssucheng, Taiping and Hsilin Districts<sup>3</sup>), Japan (Nara, Ehme, Yamaguchi near Kioto); in Australia it is found in New South Wales, Victoria, and New Zealand, New Caledonia.

### *Native Antimony.*

Native antimony occurs but rarely, and is not a source of any importance.

### *Oxide of Antimony, Sb<sub>2</sub>O<sub>3</sub>,*

otherwise known as *white antimony* or *antimony bloom*, is dimorphous: the rhombic form is named *valentinite* and the cubic form *senarmontite*; it contains 83·4 per cent. of antimony, and 16·6 of oxygen; it is formed by the weathering of *antimony-glance* or of *native antimony*, and occurs in the upper portions of antimony ore deposits. The localities where this ore occurs most freely are: Sena and Haminate in the Province of Constantine in Algiers, Borneo, and Sonora in Mexico.

The other antimony minerals occur in comparatively small quantity and do not constitute the basis for special processes. Among these are:—*red antimony ore*, also known as *antimony blende* or *pyrostilbite* ( $2\text{Sb}_2\text{S}_3 + \text{Sb}_2\text{O}_3$ ), containing 75 per cent. of antimony, 20 of sulphur, and 5 of oxygen, and found in Tuscany, Canada (Southam), Braunsdorf (Saxony), and Przibram; *antimony ochre* or *cervantite* ( $\text{Sb}_2\text{O}_4$ ), occurring in Tuscany. Antimony is also a constituent of many lead-, copper-, and silver-ores, especially the latter. Among these may be mentioned *bournonite*, *zinkenite*, *jamesonite*, *plagionite*, *feather-ore*, *wolfsbergite*, *polybasite*, *proustite*, *antimonial nickel*, *antimonial silver*, *miargyrite*, *berthierite*, *boulangerite*, and the *fahl-ores*. *Galena* also very frequently contains antimony.

In addition to the minerals mentioned above, the following are sometimes sources of antimony:—(1) *Speiss*, containing antimony obtained in working copper- and silver-ores which contain antimony. (2) *Residues*, &c., which contain antimony obtained in liquating antimony glance, (3) *Dross*, obtained in antimony smelting. In the working of *galena* which contains antimony, the latter metal

<sup>1</sup> *The State Mineralogist*, 1896.

<sup>2</sup> *The Min. Ind.*, 1898, p. 53.

<sup>3</sup> *Ibid.*

for the most part alloys with the lead produced, forming the so-called *hard-lead*.

### THE EXTRACTION OF ANTIMONY.

The principal source of antimony is antimony-glance; the other ores occur in too small quantity to form the subject of independent processes, and are therefore worked with antimony-glance.

The extraction is conducted principally by dry methods; proposals have been made for the use of wet processes and also of electro-metallurgical methods, but these have, as yet, not found practical application.

Antimony obtained by dry methods is always contaminated by foreign metals, and accordingly has to be refined: this is usually done in the dry way.

Sulphide of antimony is used to a large extent, especially as a paint for ships' bottoms: it is therefore the object of preparation in a special industry, which consists in simply liquating it from the other minerals and rocks which accompany it in its ores. The product of this process is called *crude antimony*; metallic antimony is known as *antimony regulus*. The liquation of antimony-glance is also sometimes the first step in the extraction of the metal, but at present is seldom resorted to, although the residues from it are worked up to extract the metal they retain. We have therefore to describe:—

I. The extraction of antimony in the dry way.

II. The proposals for extracting antimony by wet methods.

III. The proposals for extracting antimony by electro-metallurgical processes.

The production of antimony is in the hands of a few people, and whatever progress has been made in recent years is kept secret. Thus, in compiling this account, the author has had to confine himself practically to the somewhat fragmentary literature on the subject.

#### I. THE EXTRACTION OF ANTIMONY IN THE DRY WAY.

The treatment of ores containing antimony glance may have for its object, as already explained, either the preparation of crude antimony or the extraction of antimony regulus. In the latter case the product will need to be refined. We must therefore distinguish between:—

A. The treatment of antimony-glance for the preparation of crude antimony.

B. The treatment of antimony-glance and other ores of antimony for the extraction of the metal.

C. The refining of antimony.

#### A. THE TREATMENT OF ANTIMONY-GLANCE FOR THE PRODUCTION OF CRUDE ANTIMONY.

Ores containing more than 90 per cent. of antimony sulphide are used as crude antimony after being ground, without further treatment. Ores containing less than 90 per cent., and as low as 40 or 50 per cent., are subjected to liquation, if the pieces are of the right size, *i.e.*, larger than hazelnuts, best about walnut size. Small-grained ore and ores with a low percentage of antimony sulphide are, as pointed out above, worked up for the production of the metal. (Small-grained ore could be worked for crude antimony by fusion in furnaces.)

The liquation of antimony sulphide from its accompanying minerals and rock is possible on account of its comparatively low melting point, below a red heat. The maintenance of the proper temperature is of the greatest importance, for at temperatures above a red heat the sulphide is volatilised, and at too low temperatures the residues contain large quantities of antimony. The size of the pieces of ore, too, has considerable effect on the result; the smaller they are the less complete is the liquation, and the richer are the residues, and, further, fine ores lie so close together that the fused sulphide is unable to escape. The best size is proved to be that of walnuts. Fine ores with low percentage of metal give a better result if treated for the production of regulus.

In commerce great importance is attached to the radiated structure of the product: this is obtained by slow cooling of the liquated sulphide; if it is rapidly cooled this structure is absent.

The liquation can be done in closed or in open (reverberatory) furnaces. In closed furnaces the ore is contained in pots or tubes, while in the reverberatory furnace it lies exposed on the bed. The closed furnaces use more fuel, and cost more for labour, than the open ones, but they extract a larger proportion of the sulphide than the latter, which lose considerable quantities by volatilisation and oxidation. Reverberatory furnaces are preferable if the quantity to be treated is great.

## 1. LIQUATION IN CLOSED FURNACES.

The melting is done in pots or in tubes. If pots are used, they are either directly surrounded by the burning fuel or are heated by the flame from a fireplace. The latter method is always adopted where tubes are used. Pots are worked intermittently, but pipes permit the adoption of continuous work with corresponding economy in fuel.

*a. Liquation in Pots.*

*Pots directly in contact with the fuel* are used at Wolfsberg in the Harz, at Magurka, Rosenau, and Gross-Göllnitz in Hungary, at Milleschau in Bohemia, and at Malbosc in France. This method requires a high consumption of fuel, but has the advantage that it can be conducted at the mine on account of the simplicity of the furnace. It is therefore used where the ores are rich and fuel (wood or coal) is cheap at the mine.

The pots are made of fireclay, and hold from 11 to 56 lbs. In the bottom of each there are 4 or 5 holes, 0.4 to 0.6 inch in diameter, through which the molten sulphide escapes. These rest on receivers of burnt clay which collect the liquid crude antimony. The receivers, in order to ensure the slow cooling of the contents, are bedded in sand, ashes, or breeze. The pots are placed in a row, there being sometimes several of these at regular distances apart; 20 or 30 pots form one row. The space in which they are placed is enclosed by a low wall of dry masonry. The space between the crucibles and between them and the wall is filled with fuel, coal or wood being used. The liquation takes from 2 to 12 hours according to the size of the charge. At its conclusion the pots are lifted off the receivers, emptied, and again charged and placed in position. The receivers are in some places emptied after each charge and in others left till they are full. The residues contain, as a rule, not less than 12 per cent. of sulphide.

Fig. 434 shows the arrangement of an earlier liquation plant at Wolfsberg in the Harz.<sup>1</sup>

Here *a* is the pot with holes in the bottom for the escape of the liquid sulphide, *b* is the receiver surrounded with a bed of non-conducting material to prevent the rapid cooling of its contents, *m* is the wall, which in this instance encloses only one row of pots; it is built of dry masonry and is provided with draft holes. The height of the pot is about 12 inches, the diameter 8 inches, and it holds 12 lbs.

<sup>1</sup> Kerl, *Metallhüttenkunde*, p. 520.

At Malbosc (Ardèche), in France, the charge per pot is 33 lbs. After 4 charges (40 hours) the receiver, being full, is emptied. In

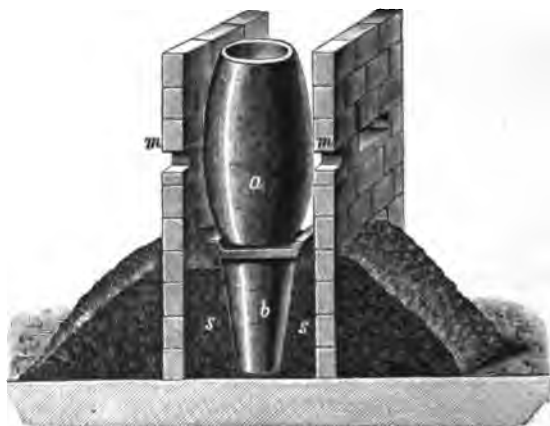


FIG. 434.

the 40 hours 20 pots produce 1,050 lbs. of the sulphide with a consumption of fuel of 3,330 lbs. of coal and 448 lbs. of brushwood.

*Pots heated by a flame* permit of greater economy of fuel and also facilitate the working of poorer ores, but the labour is more severe on the workmen than in the method previously described. These pots are placed in a furnace on each side of the fire, or are arranged in a circle round it: the receivers for the melted sulphide

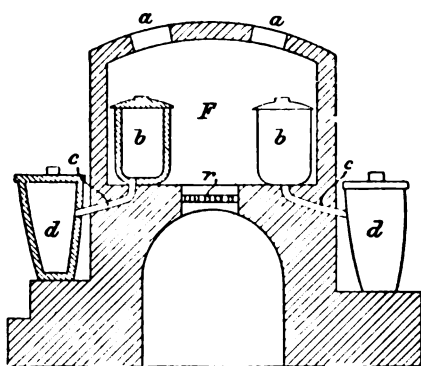


FIG. 435.

are either placed below the bed of the furnace surrounded by sand and out of contact with the flame, or they are placed entirely outside the furnace being connected with the liquation pots by a clay pipe. The latter arrangement is not more satisfactory than the former, because it does not necessitate the interruption of the process for the clearing out of the receivers as is the case

with the former. Furnaces with the receivers under the bed are employed at La Lincolle in France (Haute Loire), those with anterior receivers are used in Hungary. Fig. 435 shows the construction of one of the latter sort of furnaces:—

*F* is the heating chamber, *r* the grate, *b, b* are the pots fitted with covers, *d, d* the receivers, *c, c* the pipes connecting the pots with the receivers, *a, a* are openings in the roof through which the charges are introduced into the pots. The fuel consumption is higher and the production less in the pot furnaces, and they are inferior to the tube furnaces which are next to be described.

### *b. Liquefaction in Tube Furnaces.*

These furnaces can be arranged with vertical or horizontal tubes, but the latter arrangement does not appear to have been adopted. The vertical arrangement is used at Malbosc in France and at Sany in Hungary, and with it more favourable results have been obtained in regard to fuel consumption, quantity treated, and cost of labour, than with the pot furnaces.

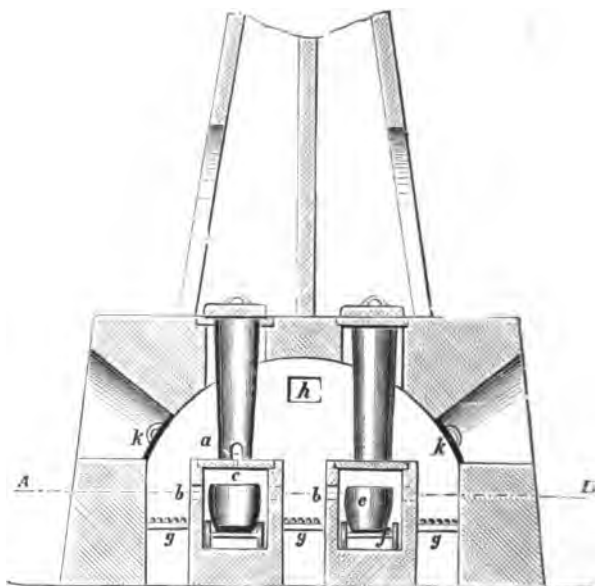
The construction of the furnace used at Malbosc is shown in figs. 436 and 437.<sup>1</sup>

The tubes are arranged in groups of four, each group being placed in a chamber with 3 grates: they extend to the outside of the furnace, where they are closed, while working, with a cover, and are 3 feet 6 inches high, 10 inches diameter at the upper end, and 7½ inches diameter at the bottom, their walls being 0·6 to 0·8 inch thick. They rest on a fire-clay slab pierced with holes for the escape of the liquid sulphide; *a* in the figure is a hole in the side of the tube at the lower end through which the residue is cleared out: these holes are 2·7 inches in width and 4·7 inches high, and during the working the charge is closed with a clay plug or with a luted plate. *e* is the receiver, 1 foot 4 inches high and 10 inches wide. These, carried on small waggons, are introduced through the openings with tight fitting doors *i, i*, into the chambers shown in the figure: when full they can be replaced by empty receivers without interrupting the operation. The doors *i, i* are provided with peepholes through which the progress of the liquefaction can be observed. The flames play round the tubes and escape through three openings, *h*, into the chimney; the doors are provided with dampers by which the intensity of the fire can be regulated. Part of the fire passes through the holes *b, b*, 4 inches square, in the walls of the receiver chambers, and maintains the mass and the collected sulphide at the proper temperature. The openings *k, k* serve for the removal of the residues from liquefaction, and for repairing any damage to the tubes. During the working these are closed by cast-iron plates. A newly built furnace requires to be

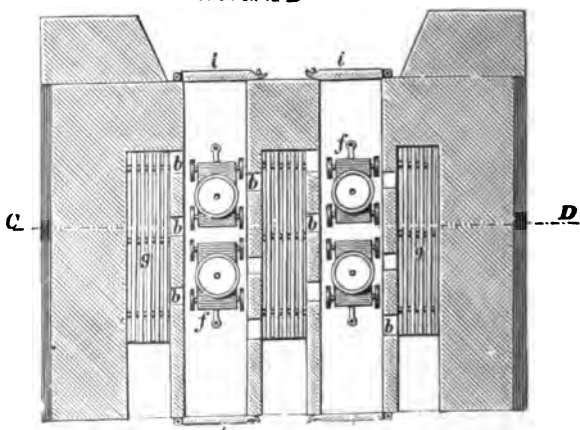
<sup>1</sup> Plattner-Richter, *Hüttenkunde*, p. 6.

heated to a bright red heat for 48 hours before a charge is inserted. The regulation of the temperature is adjusted according to the colour

*Section on C D*



*Section on A B*



FIGS. 436 and 437.

of the product, which ought to be bluish; a red colour is an indication that the heat has been too great.

The charge for each tube is 5 cwts. of ore, and it takes 3 hours



or complete liquation; the yield is 50 per cent. of sulphide. For the reduction of 100 cwts. of sulphide, 64 cwts. of coal are necessary; the tubes last 20 days each. The cost of producing 100 kilos. of sulphide is, for labour, 1·53 francs (=7·4*d.* per cwt.), and for fuel, 2·28 francs (=6*d.* per cwt.); while the cost in pot furnaces is, for labour, 2·21 francs, and for fuel, 6·34 francs per 100 kilos. (=10½*d.* and 2*s.* 8*d.* per cwt. respectively).

## 2. LIQUATION IN REVERBERATORY FURNACES.

This method of liquation possesses the merit of being the least expensive in fuel, labour, and repairs, but it leads to considerable loss of sulphide by volatilisation. It can, therefore, only be adopted where it is a question of producing large quantities of crude antimony with great rapidity, where fuel is dear, and where the cost of mining the ore is low, and therefore loss of sulphide may be disregarded.

The liquation furnace may be constructed like that for the removal of lead from copper, or like the German refining furnace. In the latter case, a tap-hole must be introduced at the deepest point of the bed. The liquated sulphide will escape through the tap-hole into the receiver placed in front of it. Towards the end of the process the tap-hole is closed, and the furnace strongly fired. The sulphide still in the ore now collects below the layer of slag which forms, and is tapped. The slag is afterwards withdrawn through a side door.

### *Products of Liquation.*

These are crude antimony and liquation residues. Crude antimony is frequently contaminated by the presence of arsenic sulphide, lead sulphide, and iron sulphide. The extent of this contamination may be seen from the following analyses of sulphides from Hungary:—

	Rosenau.	Liptau.	Magurka.	Neusohl.
FeS . . . .	1·102	4·093	—	} 3·235
PbS . . . .	—	—	—	
As <sub>2</sub> S <sub>3</sub> . . . .	0·568	3·403	—	0·247
Cu . . . .	—	—	0·59	—
Pb . . . .	—	—	3·75	—
Fe . . . .	—	—	2·85	—
	<hr/> 1·670	<hr/> 7·496	<hr/> 7·19	<hr/> 3·482

The liquation residues contain up to 20 per cent. or even more of sulphide of antimony; it is contained, not only in the interior of the pieces but also covers them as well, in the form of a thin glaze.

The following analysis shows the composition of these liquation residues<sup>1</sup>:—

$\text{Sb}_2\text{S}_3$	20.40
$\text{FeS}$	2.87
$\text{FeS}_2$	1.23
$\text{SiO}_2$	59.84
$\text{Al}_2\text{O}_3$	4.65
$\text{CaO}$	5.22
$\text{CO}_2$	4.10
Alkali and carbonaceous matter	1.69
	<hr/> 100

The liquation residues, when sufficiently rich, are worked up for antimony regulus.

#### B. THE TREATMENT OF ANTIMONY-GLANCE AND OTHER ANTIMONY ORES FOR THE EXTRACTION OF METALLIC ANTIMONY.

The treatment of antimony-glance for the extraction of metallic antimony can be done either by the roasting and reduction method or by the precipitation method.

The former consists of an oxidising roasting of the ore, followed by a reduction of the oxide formed during the roasting, by means of coal, with the addition of fluxes and covering materials (soda, potash, glauber salt). The process may be performed in shaft furnaces, reverberatory furnaces, or (in rare instances) in pot furnaces.

The precipitation method is carried out by smelting antimony-glance (or crude antimony) with iron and fluxes. The antimony is separated in the metallic state with formation of sulphide of iron. It may be done in pot, or in reverberatory, furnaces.

Antimony cannot be won from antimony-glance by a roasting and reaction process similar to that used in the preparation of lead from galena, since the sulphide and oxide of antimony are not decomposed mutually on heating as are sulphide, oxide, and sulphate of lead; sulphide and oxide of antimony melt with decomposition to form a glass of oxy-sulphide. Antimony tetroxide is only reduced by antimony sulphide to the trioxide, and antimony glass is formed at the same time.

<sup>1</sup> Hering, in *Dingler*, vol. ccxxx., p. 253.

The roasting and reduction method is less expensive than the precipitation method, and is suited to the working of poorer ores and liquation residues; it is therefore to be preferred to the precipitation method. The latter is only suited for the smelting of rich ores and of crude antimony, and is more expensive in practice, on account of the high coal consumption and labour cost; it is only rarely adopted.

The antimony ores, other than antimony-glance, are not treated by independent special methods. When sulphuretted, they are worked together with antimony-glance. If they are oxidised ores, they are subjected to a reduction process, *i.e.*, they are mixed with antimony-glance after it has been roasted.

### 1. THE ROASTING AND REDUCTION PROCESS.

This may be resolved into (1) the roasting of antimony-glance, and (2) the subsequent reduction of the oxide of antimony formed in roasting.

#### *a. The Roasting of Antimony-Glance.*

The roasting of antimony-glance can be so conducted that the product shall principally consist of either the stable tetroxide or the volatile trioxide; in the latter case the trioxide would be collected in a suitable arrangement for condensation. The former method of roasting is more usual; the latter, which has been named "volatilising roasting" (*verflüchtigende Röstung*), has been suggested for the extraction of antimony oxide of antimony, and has, in fact, come into use.

The chemical changes which take place during the normal oxidising roasting of pulverised antimony-glance, having for its object the conversion of the sulphide into the tetroxide, are the following, if the correct conditions of temperature and air admission are observed:—

When the temperature is raised to the proper point (not much over 350°C.), the atmospheric oxygen converts the antimony trisulphide into sulphur dioxide and antimony trioxide. A part of the latter is further oxidised to the pentoxide, and this, combining with some of the trioxide, forms the tetroxide. Antimonic acid is formed in the presence of oxides of metals, and combines with them to form antimoniates. Furthermore, if the oxides of metals which are inclined to form antimoniates are present, a portion of the trioxide, in the presence of air, and in contact with the foreign oxides, is changed into antimonic acid, and forms antimoniates. No formation of

sulphate of antimony takes place. If the ore contains large quantities of foreign sulphides, which on being calcined would form sulphates, antimoniates of the foreign metals are formed instead of the sulphates.

With pure antimony-glance, and the correct temperature and quantity of air, the product of roasting is principally the tetroxide, but it always contains antimony glass and undecomposed sulphide. If there are foreign sulphides and arsenic compounds in the ore, antimoniates, arseniates, and sulphates of the foreign metals are found in the roasted mass.

Since antimony sulphide and antimony trioxide melt at a dark red heat and form antimony glass, and since, furthermore, they are both volatile, the maintenance of the proper temperature is of the greatest importance. According to Bidou it is not allowed to exceed about  $350^{\circ}\text{C}.$ ; at lower temperatures the sulphide would not be decomposed. At temperatures only slightly beyond  $350^{\circ}$ , the mass begins to frit together, thereby preventing the penetration of air to the interior. At still higher temperatures the trioxide volatilises.

By regular rabbling, the fritting of the mass during roasting is prevented even at the higher temperature; and the presence of gangue in the ore also tends to obviate this difficulty. The richer the ore, the more difficult it is to roast it; with rich ores it is impossible to prevent to some extent both the liquation of a portion of the sulphide and the formation of flue dust, which latter consists almost entirely of antimony trioxide and tetroxide, antimony sulphide, arsenic compounds, and carbonaceous matter. It is therefore only possible to raise the temperature for the purpose of oxidising any unaltered sulphide, after the greater part of the sulphide has been converted into tetroxide. Properly roasted ore should appear of a reddish colour while in the furnace, and of an ashy grey colour on cooling; further, while in the furnace it should feel soft under the rabble, and free from any fritting together. If the admission of air during the roasting be limited, the volatile trioxide and not the tetroxide is formed.

The so-called *volatilising roasting*, which is only designed to form and volatilise the trioxide, requires for its execution a restricted air supply and a higher temperature. Steam at a high temperature also effects the formation of the trioxide, with the simultaneous production of sulphuretted hydrogen. This method of roasting was proposed for the treatment of poor ores and residues from the liquation of crude antimony, and is used in France for ores containing 7 to 8 per cent. of antimony. Since the arsenic contained in the

ore, when roasted, forms compounds which are more volatile than antimony trioxide, it is possible to separate the two products by intercepting the latter. This method of roasting also has the advantage that the gold and silver, which nearly always exist (with other metals) in these ores, remain in the residue and can be extracted.

*The Execution of the Ordinary Roasting.*

Ordinary roasting (i.e., for the production of the tetroxide) is carried out in reverberatory furnaces which are provided with arrangements for condensation.

Formerly (1862), muffle furnaces were in use in Hungary. The reverberatory furnaces now in use are of two kinds:—

1. *Rabble-furnaces* (intermittent working).
2. *Long-bedded hand-furnaces* (*Fortschaufelungsofen*).

*Rabble-furnaces* were formerly in use at Bouc and Septèmes in the department of Rhône in France, and are still used at Siena in Tuscany.

The latter furnaces are used in, among other places, New Brunswick, and at Banya in Hungary. They are worked with less cost for fuel and labour than the rabble-furnaces.

The arrangement of the earlier pattern of rabble-furnace with two fireplaces, as used in France, is shown in Figs. 438 and 439.<sup>1</sup>

The horizontal bed *h* is egg-shaped and is 8 feet 3 inches long, with a greatest width of 4 feet 7 inches; *r, r* are the two fireplaces, one on each side of the bed, 5 feet 3 inches long and 1 foot 2 inches wide. The gases from the fire pass through the opening *F* in the roof into the flue and through the latter into the chimney *E*. *A* is the working door; *S* is a hood built above the working door, which draws away the antimonial fumes from the furnace-men.

In these furnaces 5 to 6 cwts. of ground and sifted ore are roasted in 6 hours; during the first 2 hours the working door is closed; after that it is opened, the charge well stirred, and constantly rabbled till the finish. The loss of antimony in properly executed roasting amounts to only 2 per cent.

At Siena <sup>2</sup> 4 cwts. of fine ore are charged at one time, and the roasting requires 3 to 12 hours according to the richness of the ore; ores rich in antimony require a much slower roasting than those which are poor. The consumption of fuel (lignite) per charge is on the average 77 lbs., and the loss of antimony is 5 per cent.

<sup>1</sup> Kerl, *Metallurgy*, p. 524.

<sup>2</sup> Bidou, *L'Antimoine en Toscane*. *Genie civil*, 1882.

The *Fortschauelfungssofen*, used in New Brunswick,<sup>1</sup> is 42 feet 6 inches long, 7 feet 6 inches wide, and has 10 working doors in either side. The height from bed to roof is 2 feet 1 inch, and the fire-grate is 2 feet 1 inch wide. The firebridge is 5 feet 2 inches high and 1 foot broad. There are 5 charges of 6 cwt. each in the furnace at one time. During 24 hours, 3 charges (18 cwt.) are drawn, so each charge remains in the furnace 40 hours. During the last 2 hours before being drawn, the ore is strongly heated and rabbled every 5 minutes. Properly roasted ore has a dull, greyish-yellow

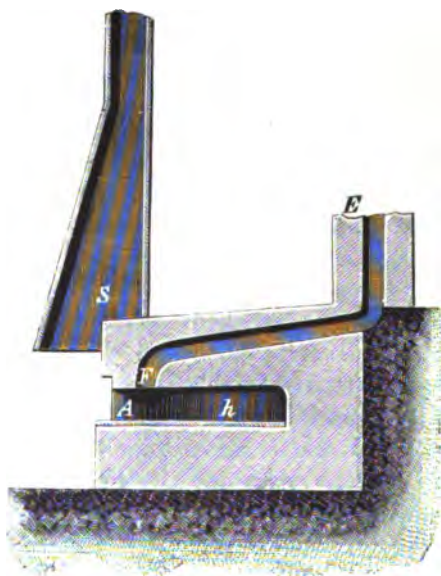


FIG. 438.

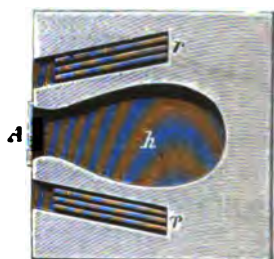


FIG. 439.

colour. The consumption of wood is three-quarters of a cord in 24 hours, and the loss of antimony is stated to be 7.5 per cent.

Similar furnaces at Banya are 26 feet 3 inches long, 6 feet 6 inches wide, with 5 working doors in one side. Charges of 4 cwt. each are introduced at the end of the furnace farthest from the fire and are drawn after 20 hours; 24 cwt. are roasted in 24 hours. The fuel is lignite, which is burnt in a stepped grate.

Furnaces have been proposed with a trough-shaped bed sloping towards one of the longer sides of the furnace, the object being to perform the reduction and roasting in the same furnace. Since the liquation of a certain portion of the sulphide cannot be avoided

<sup>1</sup> *Engineering and Mining Journal*, 1873, vol. xvi., No. 25.

during the roasting, this arrangement allows it to be tapped off and sent to market as crude antimony.

### *Volatilising Roasting.*

This method, as already pointed out, was proposed by Hering for the treatment of poor ores and residues from the manufacture of crude antimony. The ores, or residues, as the case may be, are roasted in a reverberatory furnace at a temperature sufficiently high to volatilise the antimony trioxide, which is collected in condensing chambers; it is said to be very pure and to yield on reduction a very pure metal.

If the oxide is to be used as a pigment, a very limited application of it, it must be of exceptional whiteness, and to ensure this the roasting is conducted in muffles. At the works at Conches, in the Cantal and Bironde in the Haute Loire,<sup>1</sup> ores containing 7 to 8 per cent. of antimony are subjected to a volatilising roasting in furnaces not described in detail. The antimony oxide, which is collected in condensers, is said to be free from all but traces of  $\text{Sb}_2\text{O}_4$  and  $\text{Sb}_2\text{O}_5$ , and is used partly for the preparation of paint, and partly for reduction by smelting it with coal and slags containing alkalis. The metal thus produced contains 90.94 per cent. of antimony. Oehme obtains pigment with great purity of tint by roasting the sulphide in a restricted air supply with admission of steam; this is said to produce an oxide of great purity in white sublimed needles, sulphuretted hydrogen being formed at the same time. The steam is introduced by allowing water to drop into the muffle, and the air enters by a small opening at the front.

The construction of the plant is seen in Figs. 440 and 441.

*M* is the muffle, *L* is the opening for the admission of air. The water enters the muffle at *w*, flowing along the tube *R* fitted with a cock. The gases and vapours pass out of the muffle through the pipe *x* along the pipe *y* into the condensing chambers *z*, after which they enter the scrubber *s* through the horizontal pipe shown in the figure. The scrubber is supplied with a flow of water which condenses the last portions of trioxide. The incondensable gases pass out of the scrubber along the iron flue *v*; *m* is the firedoor, *n* the door of the ash-pit. After the fire gases have passed round the muffle, they also enter the flue *v*. The chambers are emptied by means of the door *T*.

The supply of water must be regulated so that neither the vapour

<sup>1</sup> *The Min. Ind.*, 1902, p. 36.

of trioxide nor the sublimed product are moist, otherwise the sulphuretted hydrogen present would re-convert the oxide into sulphide. Excess of air would lead to the formation of the tetroxide and sulphur dioxide, the former of which would remain in the muffle.

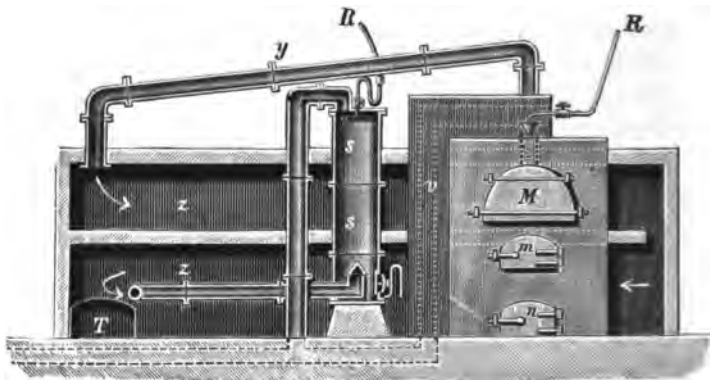


FIG. 440.

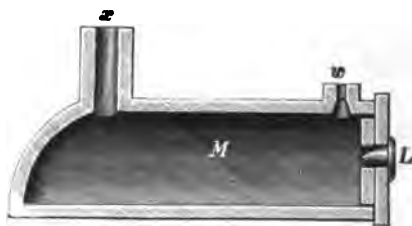


FIG. 441.

A dark red heat is best for obtaining a satisfactory result. The author is not acquainted with the practical results of working this process.

#### *b. The Reduction Process.*

The object of this is to reduce the oxide (either tetroxide or trioxide) to metallic antimony or regulus of antimony. If coal alone be used for this purpose, a large proportion of the antimony will be lost through volatilisation as trioxide, and any antimony sulphide still remaining in the roasted ore will not be decomposed. Substances are therefore added to the charges, which, on account of their easy fusibility, form a protecting cover and prevent the volatilisation of the antimony: these also assist in the formation of fusible slags, and separate the metal from any sulphide of antimony present. The substances which are most advantageous for this purpose are such as remove the impurities from



the antimony and also serve as a refining medium. Potash, soda, glauber salt, and other alkaline substances are used.

The reduction is carried out in reverberatory furnaces, in shaft furnaces, and occasionally in crucibles in pot furnaces.

*The reverberatory furnace* process is simple and easily controlled, but is accompanied by considerable loss of antimony, and is therefore only used where ores are rich and raw fuel cheap. Antimony tri-oxide formed in the volatilising roasting is reduced to regulus of antimony in pots.

*The shaft furnace method* causes less loss of antimony than the former one, and is less expensive, but presents technical difficulties. It is necessary to form a protecting slag which shall be sufficiently thin and fusible to protect the separated antimony from volatilisation and from oxidation by the air blast. It may be employed for ores which are too poor in antimony to be smelted in reverberatory furnaces.

Antimony ores are only exceptionally heated in crucibles, as the cost of fuel and labour is very high. The oxide, however, is reduced in these, as stated above.

#### *Reduction in Reverberatory Furnaces.*

The loss of metal with these furnaces is high, amounting at the least to 12 per cent.; indeed, Helmhacker says it may rise as high as 30 or 40 per cent. This pattern of furnace is (or was) in use at Bouc, at Septèmes, at Siena, in Upper Hungary, and also in New Brunswick.

At Bouc and Septèmes the roasted ores are worked up together with oxidised ores from Algiers, and with antimonial flue dust.<sup>1</sup> The furnace-beds are egg-shaped, 7 feet 10 inches long, 5 feet 3 inches wide in the centre, and 3 feet 4 inches wide at the fire-bridge. The bed is a deep hollow one, built of fire-brick, and slopes from every part to the tap-hole in one of the longer sides. The tapping-pot is placed below the tap-hole, level with the floor of the shed. The height from the bed to the centre of the roof is 3 feet 3 inches. The construction of the furnace is shown in Figs. 442 and 443.

*H* is the bed, *o* the opening by which the charge is introduced, which is 1 foot 4 inches wide, *x* is the opening through which the charge is worked, *y* is the tapping-pot; *F* is the fire-bridge, the top of which is 1 foot 4 inches above the fire-bars, and 1 foot below the roof;

<sup>1</sup> Simonin, *Bull. de la Société de l'Industrie*, vol. ii., bk. 4, p. 577.

*r* is the fire-place, *p* the roof; *z* is the flue, 8 inches in diameter, connected with condensing chambers 400 feet long for the deposition of the antimonial vapour. At the end of the system of condensing chambers is the main chimney. The dust obtained from these chambers contains up to 50 per cent. of antimony. The charge for this furnace consists of 400 to 500 lbs. of roasted ore, oxidised ores and flue dust, 90 to 110 lbs. of a flux consisting of salt, smaller quantities of soda, and sometimes a small quantity of glauber salt, 65 to 75 lbs. ground charcoal, and 220 to 330 lbs. of slag from the previous charge: this slag contains principally common salt.

The fluxes are introduced into the furnace first, and fired; when in a state of tranquil fusion, about an hour after charging, the introduction of the other ingredients of the charge is commenced. These are

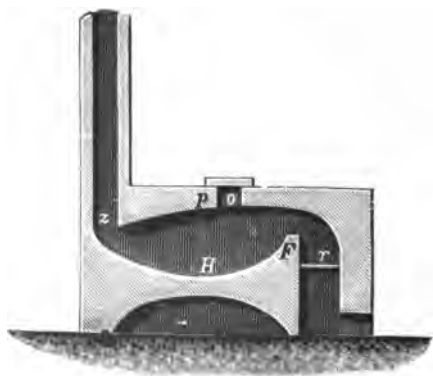


FIG. 442.



FIG. 443.

added through the working door in portions of about 44 lbs. at intervals of 15 minutes and well stirred in. After the addition of each portion a scum is produced, which is drawn off through the working door. When the last portion has been added and stirred in, the furnace is strongly fired, and the charge tapped, the whole process occupying from 4 to 6 hours. During the process the antimony is separated from its oxygen and sulphur compounds by the action of the charcoal and soda, gangue is slagged by the soda, and the foreign metals present are carried into the slag as sulphides by the action of the sulphide of soda resulting from the reduction of glauber salt by the charcoal. The salt added to the charge acts, like the glauber salt and soda, as a flux and as a cover, but it also conveys some of the foreign metals into the slag in the condition of chlorides.

The fuel consumption is 5—6 cwts. per charge, and the loss

amounts to 14 or 15 per cent. of the total antimony contained in the ore.

The slag and metal collect in the tapping-pot, and after they have become solid are lifted out together, after which the antimony regulus is freed from slag and broken up.

At Siena the procedure resembles that practised formerly at Bouc and Septèmes.<sup>1</sup> The following are the figures obtained from the working of 830 charges<sup>2</sup>:—

368,838	lbs.	of roasted ore.
268,918	„ „	sea salt.
12,641	„ „	soda ash.
88,628	„ „	glauber salt.
38,205	„ „	slag from previous charges.
4,409	„ „	iron slag.

Antimony obtained 113,573 lbs. The loss of antimony is not given.

In New Brunswick the furnaces are 8 feet 6 inches in diameter; the beds are built of fire-clay and are concave; the depth in the centre is 1 foot 6 inches. The refining follows immediately after the reduction; the roasted ore, 5 cwts. at a time, is spread on the red-hot bed, and covered with 1 cwt. of glauber salt, and 82 lbs. of coarsely powdered hard wood charcoal. After 4 hours the charge is melted and effervescing; the carbonic oxide which is liberated escapes through the layer of slag and burns. The charge is rabbled until it ceases to boil, and then allowed to settle for half an hour. After this the charge is cooled by leaving the fire door open. When the slag has attained a low red heat and is in a pasty condition, it is drawn out, and the materials for refining are added; the furnace is then strongly heated. The added materials are 27·5 lbs. of glauber salt and 11 lbs. of wood charcoal. Sulphide of soda is formed, and produces a slag with the impurities in the antimony. After an hour and a half the metal and slag are in a state of tranquil fusion, and the melted mass is ladled into iron moulds. The pouring is done in such a way that at least half an inch of thick slag remains on the surface of the metal in the mould. In this way it is impossible for the antimony to begin to solidify before the mould is filled. As soon as the ingot is solid, the slag is removed: it is essentially a sulpho-salt of antimony mixed with sodium carbonate, and contains 15 per cent. of antimony; the latter is

<sup>1</sup> Bidou, *loc. cit.*

<sup>2</sup> Knab, *Métallurgie*, p. 528.

recovered by smelting the slag with one-fifth of its weight of iron. Information as to the amount of loss in the process is not published.

In Hungary at one works they are said to combine the refining with the reduction. It is said that 5 cwts. of roasted ore are smelted with 10 per cent. of small coal and 3 to 6 per cent. of glauber salt<sup>1</sup> in reverberatory furnaces for 20 hours; the slags are then removed and 22 to 25 lbs. of slag from a previous refining of antimony added. After this is fused, the ladling of the metal is proceeded with.

### *Reduction in Shaft-Furnaces.*

This method, as well as the reverberatory furnace method, was practised formerly at Bouc and at Septèmes in France, and at Oakland in California: at the present time it is in use at Banya in Hungary.

At Bouc and Septèmes<sup>2</sup> ores containing 30 to 40 per cent. of antimony were roasted in reverberatory furnaces and smelted in three tuyered shaft furnaces which were worked on the "*Spur*" principle with covered "eye." They were 10 feet 10 inches high. 2 feet 7 inches to 3 feet in depth, and 1 foot 11 inches wide. No information is available as to the composition of the charges. In 24 hours 2 to 2½ tons of ore were worked, and the coke consumed was half the weight of ore. The crude metal produced contained 92 to 95 per cent. of antimony and was refined.

At Oakland in California, in 1882, oxidised ores were worked in a circular water jacket furnace. The proportions of ore, etc., in the charge were 80 parts by weight of ore, 100 of slag, and 30 of coke. There was no satisfactory arrangement for condensation, and the yield of antimony was only 77½ per cent. of the assay value of the ore.

At Banya<sup>3</sup> the materials for the production of antimony were:—

Roasted ore containing . . . .	48–49 per cent. of antimony.		
Unroasted oxidised ores . . . .	46	"	"
Unroasted liquation residues from the production of crude antimony containing . . . . .	21·4	"	"
Roasted residues containing . .	23	"	"
Flue-dust . . . . .	56	"	"
Refinery slag . . . . .	25	"	"

<sup>1</sup> *Berg.- und Hütten-Ztg.*, 1862, p. 408.

<sup>2</sup> Simonin, *loc. cit.*

<sup>3</sup> *Stahl und Eisen*, 1886, vol. vi. p. 62.

These are smelted together in shaft furnaces 19 feet 7 inches high, the diameter being 4 feet 7 inches at the mouth and 3 feet 4 inches at the tuyere: each furnace has 5 water tuyeres and is constructed with a closed crucible; 3,000 cubic feet of blast are supplied per minute at a pressure of 12 inches of water. A campaign or "run" lasts 3 weeks. The charges are of two different compositions A and B. below, two charges of A alternating with one of B.

	A. Lbs.	B. Lbs.
Roasted ore . . . . .	1,213	1,323
Roasted residues from liquation . . . . .	1,654	1,323
Ore moulded into lumps with lime . . . . .	441	—
Flue-dust do. do. . . . .	220	—
Unroasted ore . . . . .	—	220
Oxidised ores . . . . .	—	220
Unroasted liquation residues . . . . .	—	220
Limestone . . . . .	1,323	1,764
Foul slags from same work . . . . .	882	882
Slags from refinery . . . . .	—	441
Impure antimony (III. below) . . . . .	—	220

The mixing of lime with the fine ore and flue-dust is only done during the first 8 or 10 days of the campaign; after that time they can be added in their pulverulent natural state without prejudice to the process. The quantities of lime used at first are, for fine ores 0 per cent. by weight, and for flue-dust 7 per cent.

In 24 hours a total of 30 cwts. is put through the furnace. The refined antimony obtained is of 3 grades, of the following compositions:—

	I.	II.	III.
Antimony, per cent. . . . .	90·02	73·80	65·04
Iron „ . . . . .	6·23	16·66	23·80
Sulphur „ . . . . .	2·85	8·42	10·46
	99·10	98·88	99·30

	Per cent.	Per cent.	Per cent.
Proportion of total output . . . . .	82·5	9·0	8·5 = 100

The grades I. and II. are refined: the grade III. is returned to the furnace in the charges as shown above.

The slags produced in this operation have the following composition:—

	I.	II.
SiO <sub>2</sub> . . . . .	46·9	45·9
CaO . . . . .	34·6	31·4
FeO . . . . .	15·1	19·9
Sb . . . . .	0·5	0·9

Slags which are not clean and contain large quantities of antimony are returned to the furnace.

Hering<sup>1</sup> proposed to work the liquation residues of the composition shown on p. 566 in a circular shaft furnace of the following

<sup>1</sup> *Dingler*, vol. ccxxx., p. 253.

dimensions, height 19 feet 8 inches, diameter at the tuyere level 3 feet 4 inches, number of tuyeres 3, blast 530 cubic feet per minute at a pressure of 7·8 inches of water. He claimed that in a furnace of this description it would be possible to smelt 7 tons of residues with the addition of 150 per cent. of tap cinder, 40 per cent of limestone, and 5 per cent. of gypsum or glauber salt, with a coke consumption equal to 14 per cent. of the weight of the residues.

### *Reduction in Pot Furnaces*

The reduction of roasted ores in crucibles and pot furnaces is on account of its high cost, only adopted occasionally where a small quantity is required, and where rich ores or crude antimony or volatilised antimony trioxide are available.

The roasted ore is fused with 10 per cent. of its weight of crude argol or with charcoal or anthracite and potash or soda, in fire-clay crucibles heated in a wind furnace or in a galley furnace. The melted metal is cast in iron moulds coated with tallow or thin fire-clay cream.

According to Knab<sup>1</sup> each crucible contains 26·5 lbs. of roasted ore with 10 per cent. of charcoal and 7·15 per cent. of salt or soda. The pots are arranged 10 or 12 in each furnace, and each pot turns out 4 or 5 charges in 24 hours. The consumption of coal is 70 to 80 per cent. of the weight of the ore, and the life of each pot is 7 or 8 charges.

## 2. THE PRECIPITATION METHOD OF REDUCTION

This method is applicable only to rich ores and crude antimony. It consists in replacing the antimony in the sulphide of antimony by iron, thus separating the antimony in the metallic state, and forming sulphide of iron at a comparatively low temperature. It is impossible, however, to completely separate the sulphide of iron from the antimony, on account of the high specific gravity of the former, and therefore sodium sulphate and carbon are added in order to produce sodium sulphide, which forms with the iron sulphide a fusible slag of low specific gravity which easily separates from the antimony. Common salt is used in England instead of sodium sulphate and carbon. Iron is best used in the form of turnings, shavings, or tin-plate cuttings. In the case of the last the tin they contain does no harm. The proportion of iron must not be too high in the case of ores containing sulphides of lead and arsenic, because the antimony would not only be contaminated with iron, but also with

<sup>1</sup> *Métallurgie*, p. 524. Paris, 1891.

the lead and arsenic reduced by the iron from their respective compounds.

With reference to this it must be borne in mind that where sodium sulphate and carbon are used, part of the iron is consumed in decomposing the sodium sulphate. It has been found by experiment that where 10 per cent. of glauber salt and 2 to 3 per cent. of coal are used, 44 per cent. of iron is required; this figure is given by Karsten, but Liebig states that 42 per cent. is sufficient, and Hering uses only 40 per cent. Berthier uses the following proportions: sulphide of antimony 100, forge scale 60, soda 45 to 50, coal dust 10. The iron in all cases separates out as the monosulphide  $\text{FeS}$ , or, according to Schweder, as the sulphide  $\text{Fe}_3\text{S}_7$ .

In England it is usual to add excess of iron in order to secure the separation of all the antimony in the ore: this however is only done with ores which are free from lead and arsenic. The excess of iron alloys with the antimony, and is removed by subsequent fusion with more sulphide of antimony.

There is some loss of antimony in the precipitation method owing partly to volatilisation of the sulphide and partly to the fact that the slags carry some away: Karsten states that the yield where crucibles are used is 64 per cent., Berthier 65 to 67 per cent.: the theoretical yield is 71.5 per cent.

This method is carried out, as a general rule, in pot furnaces, but reverberatory furnaces are sometimes used in spite of the inevitable loss of antimony; shaft furnaces have only been applied experimentally; crucible furnaces are adopted in England, Hungary and other places.

In English works, of which the principal ones are Messrs. Cookson and Co., Newcastle-on-Tyne, Messrs. Hallet and Fry, Johnson and Matthey, and Pontifex and Wood in London, ores containing 50 to 55 per cent. of antimony are worked.<sup>1</sup> An antimony-iron alloy is first produced by fusing the sulphide in graphite pots with excess of wrought iron. This ensures the extraction of all the antimony contained in the ore. This alloy is then freed from the iron it contains by fusing it in graphite pots with sulphide of antimony, and the metal obtained again fused with suitable materials in graphite pots in order to refine it. All three operations take place in the same furnace. The ore, broken to the size of hazelnuts, is smelted with wrought iron, tin-plate cuttings, salt and slag from the same process, or with skimmings from a subsequent one. Each pot holds a charge

<sup>1</sup> *Journ. Soc. Chem. Ind.*, Jan., 1892; *English Mining Jour.*, March 12, 1892; *The Mineral Industry*, 1892, p. 23.

consisting of 46.3 lbs. of ore containing 50 per cent. of antimony, 17.6 lbs. of iron, 4.4 lbs. of salt and 1.1 lb. of slag or skimmings. The iron usually consists of 14.3 lbs. of cuttings compressed into a cake and 3.3 lbs. of turnings and borings. The ore, salt, slag or skimmings, as the case may be, and the borings are mixed together and placed in the pot, and the cake of cuttings is placed on the top as a cover.

The furnaces in the largest works each contain 42 pots, which are heated by the flame from two fireplaces, one in each of the short sides of the furnace. In the centre of the roof is a flue which carries away the gases from both fireplaces. The bed of the furnace, including the two fireplaces, is 54 feet long and 7 feet 4 inches wide; the roof is low and in it are 21 openings along each long side, through which the crucibles are put in and taken out. These openings are 14 inches in diameter and are fitted with covers. The sides and roof of the furnace are covered with cast-iron plates, and there are two smaller openings, 4 inches in diameter, in the shorter sides of the roof over the fireplaces for the removal of clinkers, &c.

The two pots nearest the fire at each end of the furnace are charged with antimony for refining.

The smelting of a charge for the production of the antimony-iron alloy takes 3 hours or a little less. When the charge is melted the contents of the pot are poured into conical moulds and a new charge is introduced. When the contents of the mould are cold, the matte and slag are removed from the surface of the antimony by beating it with a hammer, and are thrown away.

The antimony-iron alloy, technically known as "*singles*," contains 91.63 per cent. antimony, 7.23 per cent. iron, 0.82 per cent. sulphur, and 0.32 per cent. insoluble matter.

The iron in the alloy is removed, as already stated, by fusion with sulphide of antimony. To ensure the complete removal of the iron, excess of the sulphide is used. The iron sulphide separates as a matte, an equivalent quantity of antimony being set free, and common salt or sometimes soda ash is added as a cover and to flux the sulphides. The charge consists of 92.6 lbs. of broken regulus, 7.5 to 9 lbs. of liquated sulphide, and 4.4 lbs. of salt, and the same furnace is used as in the former process. The fused mass is stirred from time to time with an iron rod, and the time required for a charge is about  $1\frac{1}{2}$  hours. At the conclusion of this fusion the slag and matte are removed with an iron spoon and the contents of the pot poured into a conical cast iron mould, the matte and skimmings being added to subsequent smeltings of ore.



The metal, which at this stage is known as "*star bowls*," contains 95·53 per cent. antimony, 0·18 per cent. iron, and 0·16 per cent. sulphur. The presence of sulphur, which is due to the excess of sulphide used in the second fusion, may be recognised by the appearance of small glistening patches in the crystalline pattern on the surface of the casting.

In order to remove the sulphur and to produce the so-called "*star antimony*" the "*star bowls*" have to be further refined. To do this a fused mixture of potash and sulphide of antimony is added to the metal in a graphite crucible in the same furnace as was used in the previous operations. The charge is 92·6 lbs. of metal and 8·8 lbs. of the fluxes, the latter being added after the fusion of the metal. The pots are placed in the hottest part of the furnace as close as possible to the fire, and, when the fusion is complete, the contents of the pots are stirred with an iron rod and poured.

The consumption of coal per week for the above method of treatment is 22 tons or  $1\frac{1}{2}$  tons per shift of 12 hours. Eleven crucibles are used, on the average, per ton of antimony produced, and 35 men are required to work a furnace, as shown in this table :—

	Per side of the furnace per shift, 12 hours.	For the whole furnace per shift, 12 hours.	Per day of 24 hours.
Firemen . . . . .	1	—	4
Furnacemen . . . . .	4	—	16
Refiners . . . . .	—	2	4
Metal breakers . . . . .	—	2	4
Charge mixer . . . . .	—	1	2
Workers on day shift only, viz., one smith, one boiler and engineman, and three labourers . . . . .	—	—	5
			—
			35

The loss in this process is 10 per cent. of the antimony contained in the ore, the greater part of which is due to volatilisation during smelting. Condensing chambers are connected with these furnaces and are cleaned out four times a year, when a large quantity of white flue-dust is obtained. This contains 70 to 72 per cent. of antimony and is mixed with coal dust and smelted with charges of coke.

At Magurka, in Hungary, the precipitation method was formerly in use: pot furnaces and graphite crucibles were employed. Charges of 20 to 22 lbs. of antimony sulphide with iron, potash, and pan scale (from salt works) were treated. The process was divided into two operations.

Reverberatory furnaces are said to be in use at Linz, Schleich in Austria, many, and at Alais in France. It is impossible to prevent con-

siderable loss by volatilisation in these furnaces, and they must therefore be connected with very long condensing flues in order to collect the metallic fume. The bed too must be very tight in order to prevent leakage of the fused metal, which is very fluid. At the deepest point of the bed a tap-hole is provided for drawing off the smelted charge. The detailed results of work in these furnaces are not known to the author; in any case there must be much greater loss than in the pot furnaces.

T. C. Sanderson<sup>1</sup> charges the ore carefully into a bath of iron sulphide on the bed of a reverberatory furnace. After all the ore has been added, iron is put in to decompose the sulphide of antimony, the doors of the furnace are closed, the temperature is raised and the mass stirred. After complete decomposition the antimony is tapped, and the tap-hole closed as soon as the sulphide of iron appears. Slag is withdrawn through the working doors; sulphide of iron is removed until the bed holds its original quantity, and a new charge of ore is added. This method is said to have given good results, and has been in practice already over a year.<sup>2</sup>

Hering has experimented with shaft furnaces for the treatment of liquation residues by the precipitation method. Although his experiments were not continued as far as the attainment of a definite result, and in spite of the unsatisfactory results of previous workers it appears that this method could be carried out in shaft furnaces and that the result would be the more satisfactory the richer were the ores treated.

#### *Products of the Extraction of Crude Antimony*

These are unrefined antimony and slags. The former contain many foreign elements, more particularly arsenic, iron, copper and sulphur, as the following analyses show:—

	1.                      2.		3.                      4.		5.
Method of extraction . .	Precipitation.		By reduction of oxidised ores.		From Fahlberg's process delivered by amalgamation in the Stephan Works.
Furnace used . . . . .	Reverberatory.		Shaft furnace.		—
Analyst . . . . .	Helmhacker.		—		—
Sb . . . . .	94.5	84.0	97.2	95.0	90.77
S . . . . .	2.0	5.0	0.2	0.75	2.0
Fe . . . . .	3.0	10.0	2.5	4.0	—
Co . . . . .	}	—	—	—	1.50
Ni . . . . .					
Cu . . . . .					
As . . . . .	0.25	1.0	0.1	0.25	5.73
Au . . . . .	traces	—	—	—	—

<sup>1</sup> United States patent, Nov. 18, 1902, No. 714,040.

<sup>2</sup> *The Min. Ind.*, 1903, p. 43.

The impure antimony has to be refined.

Slags from the extraction of antimony by the roasting and reduction method consist principally of silicates, those from the precipitation method of silicates and sulphides. Some of them are thrown away and some are used in the first smelting of the ores.

#### THE EXTRACTION OF ANTIMONY FROM METALLURGICAL BYE-PRODUCTS WHICH CONTAIN ANTIMONY

The following bye-products are produced in the process of extracting antimony from its ores: liquation residues, matte, slags, refinery slags and flue-dust. These, if sufficiently rich, are added to the charges in smelting the ore; the liquation dross, however, is subjected to a preliminary roasting, and the flue-dust is intimately mixed with lime, before it is smelted. Liquation residues are also sometimes treated separately in shaft furnaces.

At the Stephan Works in Upper Hungary, antimony is extracted from the speiss, which has been desilverised by amalgamation; this speiss is obtained by smelting fahl-ores. The antimony is extracted by smelting the speiss with pyritic ores in shaft furnaces. The copper is converted into sulphide by the sulphur of the pyrites, and the impure antimony obtained is refined.

#### *c. The Refining of Antimony*

Unrefined antimony, as already stated, usually contains sulphur, iron, arsenic and copper, and frequently lead as well. These impurities, with the exception of lead, can be eliminated partly by oxidising and slagging agents, partly by sulphurising agents, and partly by chlorinating agents. Sulphur is removed by fusion with soda or potash or antimony glass (antimony oxysulphide).

Arsenic is converted by soda or potash into arseniate of soda or potash, and can thus be removed. Copper and iron are converted by sulphide of antimony into sulphides; the conversion is facilitated by the addition of soda or potash, or of glauber salt and charcoal. The sulphides of iron and copper form a slag with the sulphide of sodium, which results from the reduction of the glauber salt, and with the soda or potash present. They can also be removed easily by antimony glass.

Common salt, carnallite or magnesium chloride, when added, cause the volatilisation of some foreign metals as chlorides, and slags the others. A large quantity of antimony, however, is volatilised at

the same time, so that on the large scale this method is attended with great loss of metal.

The above-mentioned methods do not eliminate lead, because metallic antimony separates lead from its oxide or sulphide; lead can only be separated from antimony by chloridising, which causes great loss of antimony, and even then the lead is only incompletely removed.

Mitscherlich suggested that the lead should be removed from the sulphide of antimony before the latter was smelted, by fusing the sulphide with 4 per cent. of iron; by this means the whole of the lead and a comparatively small amount of antimony would be removed. From all this it is obvious that the best way to produce an antimony free from lead is to use an ore which is itself free from that impurity.

It has already been pointed out that in commerce antimony is judged by the appearance of the fern-like "star" on its surface. This characteristic is not exhibited by impure metal, nor by the pure metal if any part of the surface has been exposed during solidification, nor if the slag covering set before the metal, nor if undecomposed soda or potash come into contact (even in minute quantities) with the surface. Ingots which do not show the star must, if impure, be refined, and if pure, be recast and allowed to cool under the proper conditions. Small ingots will show only a single large star, while larger ones will show several and will have a fern-like pattern on their sides.

The refining is done either in crucibles in pot furnaces, or in reverberatory furnaces. The former method requires a greater fuel consumption, and therefore for the production of large quantities of refined antimony, reverberatory furnaces are preferred, but the loss of metal in the process amounts to between 20 and 30 per cent. At many works in England the refining is performed as a part of the process of extraction.

### 1. REFINING IN POT FURNACES

This kind of furnace is, or used to be, in use at Septèmes in France, in England, and at Oakland in California.

At Septèmes, 30 crucibles were arranged on a level bed in one furnace; the shape of the furnace being that of a barrel cut lengthways down the middle. The following were the dimensions of the furnace:—length, 7 feet; breadth across each end, 4 feet; breadth in the middle, 5 feet; the bed was 6 inches lower than the bridge.

The roof was 8 inches above the bridge, 1 foot 6 inches above the middle of the bed, and 10 inches at the end where the flue left the furnace. The dimensions of the fireplace were:—length, 5 feet; breadth, 1 foot 8 inches; depth from roof to bars, 1 foot 4 inches. The working door was placed in the front longer side and was 20 inches wide. The crucibles were made of fireclay and stood 5 or 6 charges each, each charge consisting of 48·5 lbs. of impure antimony. The flux used was a mixture of sulphate and carbonate of soda with a little salt and pure oxidised antimony ores; 13 to 17 lbs. of this mixture was added to each charge. The fusion was conducted at a low red heat and lasted 6 hours, during which time 450 to 550 lbs. of coal was used.

In England, the refining is carried out as described on p. 580. The flux used is prepared by fusing together 3 parts of potash and 2 parts of crude antimony; 8·8 lbs. of this is added to 185 lbs. of the impure metal, which must be carefully cleaned from adhering slag and matte. At the conclusion of the fusion, the contents of the pot are poured together into a conical mould; when cold the slag is easily separated from the metal. The slag is used again with the addition of a little potash. The star only appears when the surface of the cooling metal is completely covered with a quarter of an inch of slag. When the ingot is cold the slag is removed by scrubbing with water and sand.

## 2. REFINING IN REVERBERATORY FURNACES

Reverberatories are or were used at Milleschau, at Banya, at Siena, and at Oakland. It is most necessary that the furnace should have a tight bed and one which will resist the action of the fused alkalies, otherwise the metal will leak through. It is best to build it of blocks of a native fire-resisting stone such as granite; newly cut stone, however, cannot be used, partly weathered and seasoned stone being better.<sup>1</sup> If such stone is not available, a mixture of burnt and raw clay may be used, but in this case it will need to be rammed into an iron pan.

Figs. 444—446 show the construction of a furnace built by Hering at Milleschau, and used and worked successfully, and which was particularly commended by Helmhacker.<sup>2</sup>

The bed consists of a granite block *g* which is carried by three iron rollers *c*, in order that it may be easily placed in and removed from

<sup>1</sup> *Berg.- und Hütten-Zeitung*, 1883, pp. 1, 44, 145, and 172.

<sup>2</sup> *Berg.- und Hütten-Zeitung*, 1883, *loc. cit.*

the furnace. The rollers run on the three railway bars *f*. The bed is in contact with the furnace wall only at the front, or working side. There is a depression or sump in the bed at *d*, in which the antimony collects and from which it can be ladled; *b* is the working door at

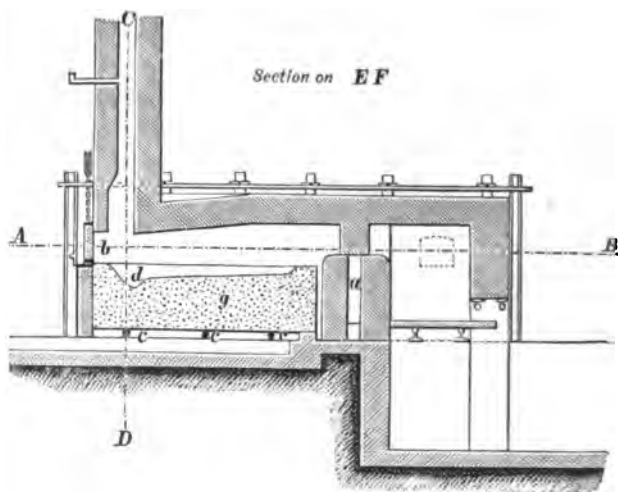


FIG. 444.

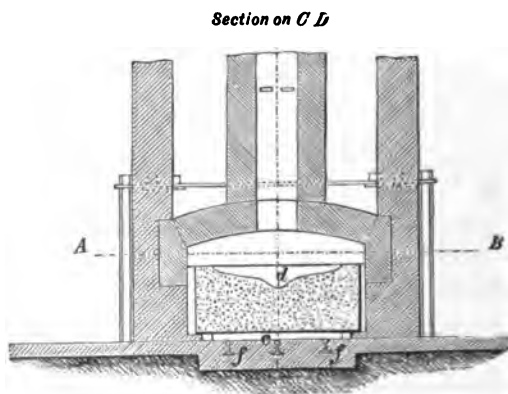


FIG. 445.

the opposite end to the firebridge. On account of the difficulty of working with only one door, the later patterns of furnace are provided with two opposite to each other, one on either side at the flue end of the furnace. One of them is used to draw the slag, and the other is used for ladling out the metal and charging. The firebridge is provided with vertical channels *a*, in which air for the complete combustion of

the fire gases can be heated. These channels are connected with a horizontal flue running through the bridge and provided with a slide, so that the amount of air admitted may be regulated. *C* is the chimney provided with a damper. The charge for a furnace of these dimensions is 1,200 to 1,500 lbs. exclusive of the fluxes.

At Banya the bed is built of fireclay 11 inches thick contained by, and well rammed into, an iron box 13 feet long and 8 feet 2 inches wide. A charge consists of 10 cwt. of unrefined metal.

In the Milleschau furnace described above, antimony which contains large quantities of impurity is refined first by soda and then by antimony glass, while the purer sorts are refined by antimony glass alone. The tetroxide of antimony used in making the glass is obtained in the form of crusts which form in the hottest part of the

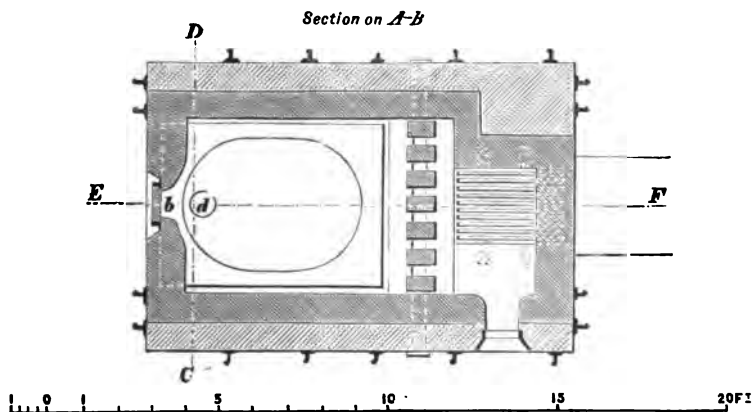


FIG. 446.

chimney. According to Helmhacker<sup>1</sup> the procedure in refining is as follows:—

The charge of 1,200 to 1,500 lbs. is thrown into the red-hot furnace as rapidly as possible, and melted in less than an hour. Vapour of antimonious and arsenious oxides are given off both during the charging and during the fusion. According to the purity of the metal from 3 to 7 per cent. of soda is added as soon as it is fused; it is well to mix a little coke-dust or fine charcoal with the soda: after this, the heat is raised to bright redness in order to fuse the soda.

The slag gradually becomes thicker and thicker till, after about 3 hours, the bubbles, which at first were numerous, rise very slowly through the charge. The slag is then very carefully skimmed off through the working door.

<sup>1</sup> *Berg- und Hütten-Zeitung*, 1883, loc. cit.

At this stage iron and sulphur are still left in the metal, and to remove these the materials for the formation of antimony glass are now added. For each 100 lbs. of antimony in the charge, 3 lbs. of liquated sulphide of antimony and  $1\frac{1}{2}$  lbs. of antimony tetroxide are thrown in, and when these are fused  $4\frac{1}{2}$  lbs. of potash or white flux are further added.

The fluxes must completely cover the bath of metal.

At the end of a quarter of an hour the antimony is pure and may be ladled, which is done with iron ladles, very cautiously, in order to secure the starred appearance of the ingots. When cold the ingots are removed from the moulds and the layers of slag broken off by means of a hammer.

Three charges of 1,300 to 1,500 lbs. each can be refined in one of these furnaces in 24 hours; the consumption of coal is 1,300 lbs. for the three charges.

The slag obtained in the last process of refining, the so-called *star slag*, consists principally of antimony glass, and contains from 20 to 60 per cent. of antimony; it is generally used over again for refining. When it becomes too impure for this purpose, it is added to charges of ore which are about to be smelted; the other slags obtained in the course of refining are also smelted with ore charges. The impurities in *star slag* are sulphides of iron and nickel, iron oxides and silica.

Loss of metal takes place in refining by volatilisation and in the flue-dust, and amounts to 20—30 per cent. Flue-dust is principally antimony trioxide and tetroxide. The cost of refining is said to be  $2\frac{1}{2}$  to 3 marks per 100 kilos (*i.e.* 1s. 3d. to 1s. 7d. per cwt.).

At Banya the charge for the furnace above described is 990 lbs. of higher grade metal (90 per cent. Sb), and 110 lbs. of the lower grade metal (74 per cent. Sb). To this are added 92.6 lbs. of sodium sulphate, 11 lbs. of powdered charcoal and 330 lbs. of raw ore. After 10 hours the slag is drawn off and the materials for forming the star slag are added, *viz.*:—2.2 lbs. of crude antimony, 13.2 lbs. of roasted sulphide of antimony, 7.5 lbs. of potash and 5.7 lbs. of soda ash. The refined star antimony which is obtained contains impurities to the following amounts:—

Arsenic . . . . .	0.330 per cent.
Iron . . . . .	0.052 „
Silver . . . . .	0.006 „
Sulphur . . . . .	0.720 „
Total impurity . .	1.108 „



At Siena, where the unrefined metal is less impure, the total weights of 260 charges are given as follows:—115,255 lbs. of unrefined metal, 27,229 lbs. of salt, 767 lbs. of roasted ore, 12,549 lbs. of refinery slag. The refined antimony obtained was 107,697 lbs., which is equal to 93·5 per cent.

### *The Products of Refining*

These are—refined antimony, refinery slag and star slag.

*Refined antimony.*—The composition of metal from different sources is seen from the following table.

	I.	II.	III.	IV.	V.	VI.
Source . . . . .	{ Lipto Szt Miklos, Hungary }	California.	California.	{ Samples for tenders at the Royal Docks at Wilhelmshaven.		
Analyst . . . . .	Hirzel.	Booth, Garret, and Blair.		Himly.		
Sb . . . . .	98·27	98·34	99·081	98·98	98·81	98·87
Cu . . . . .	0·54	0·021	0·052	0·01	0·02	0·02
Fe . . . . .	0·63	0·144	0·039	0·35	0·34	0·16
Pb . . . . .	—	0·410	0·538	0·34	0·34	0·73
As . . . . .	—	1·008	0·036	0·09	0·36	0·09
Bi . . . . .	0·36	—	—	—	—	—
S . . . . .	—	0·064	0·254	0·23	0·12	0·11
Co and Ni . . . . .	—	0·013	traces	—	—	—

*Refinery slag* contains from 20 to 60 per cent. of antimony, and is a mixture of soda, sodium sulphantimoniate, antimony trioxide and tetroxide, ferrous oxide, iron sulphide, arsenic oxide, and smaller proportions of silica and alumina; it is added to charges of ore.

*Star slag* consists principally of antimony glass, and is used repeatedly till it becomes too impure for further use in refining, when it is added to ore charges.

## II. PROPOSALS FOR THE EXTRACTION OF ANTIMONY BY WET METHODS

There have been several proposals of this nature for the extraction of antimony from poor ores and liquation residues, but as yet they have found no practical application and appear to have no prospect of adoption.

Hydrochloric acid, ferric chloride and alkaline sulphides have been proposed as solvents.

The method of Hargraves<sup>1</sup> is, to treat the finely powdered ore with hydrochloric acid, heat being applied at the same time. The solution after being neutralised with lime is to be treated with zinc

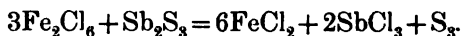
<sup>1</sup> *Dingler*, vol. cciii., p. 153.

or iron in order to precipitate the antimony. The precipitated metal is to be washed successively with antimony trichloride solution, hydrochloric acid and water, and then fused with potash in crucibles.

Smith's method is similar.

Hering also proposes hydrochloric acid as a solvent for liquation residues.<sup>1</sup> He precipitates the antimony from the solution as basic chloride by water, or as sulphide by sulphuretted hydrogen. The latter is to be obtained by digesting the liquation residues with hydrochloric acid. The basic chloride or sulphide obtained is not further treated, but is to be sent to market as such.

Rud. Koeppe & Co.<sup>2</sup> propose ferric chloride as a solvent. Sulphide of antimony reduces it according to this equation:—



The reaction proceeds well when hydrochloric acid or haloid salts are present.

E. W. Parnell and J. Simpson<sup>3</sup> have proposed alkaline sulphides as solvents.

Edwards<sup>4</sup> proposes to separate gold and silver from antimony ores containing them by digestion with a cold 7 per cent. solution of calcium sulphide, which dissolves the antimony and leaves the precious metals. By treatment of the solution of the sulphides of calcium and antimony thus obtained with carbon dioxide in closed vessels, calcium carbonate is first precipitated, and afterwards antimony sulphide. The hydrogen sulphide evolved in this reaction may be used to regenerate calcium sulphide solution by bubbling it through milk of lime.

Proposals have also been made to heat silver-bearing antimonial fahl-ores free from lime with glauber salt and coal, in order to convert the antimony into the double sulphide of sodium and antimony. This salt may then be leached out and decomposed by sulphur dioxide with formation of antimony sulphide and sodium thiosulphate, and the sulphide precipitate treated for antimony in the ordinary manner. Any silver or copper in the ore would be left behind in the residues from the leaching process.

<sup>1</sup> *Dingler*, vol. ccxxx., p. 253.

<sup>2</sup> German Patent, No. 66,547, of 12 April, 1892.

<sup>3</sup> English Patent, No. 11,882, of 1 September, 1884; *Chem. Ztg.*, 1885, p. 412.

<sup>4</sup> English Patent, July 2, 1897, No. 15,791.

## III. METHODS PROPOSED FOR EXTRACTING ANTIMONY ELECTROLYTICALLY

Although Luckow in 1880, and Classen<sup>1</sup> and Ludwig in 1885, published a method for the electrolytic determination of antimony, no method of extraction based on this principle has hitherto been adopted. It is questionable, apart from the technical difficulties, if antimony can be profitably extracted in this way.

Borchers<sup>2</sup> has proposed a method, based on his own experiments, for the extraction of antimony from ores by the use of insoluble anodes. He uses as solvent sodium sulphide, which easily dissolves antimony sulphide, and separates the antimony from the solution by means of the electric current. The action takes place best when three molecules of sodium sulphide ( $\text{Na}_2\text{S}$ ) are present for each molecule of antimony sulphide ( $\text{Sb}_2\text{S}_3$ ). If the antimony sulphide exceeds this proportion, sulphur is liberated and interferes with the action, while if sodium sulphide be in excess, the resistance of the electrolyte is increased. The strength of the solution should not exceed 9° B. when hot or 12° B. when cold, and to this 3 per cent. of salt is added. The latter promotes the separation of the dissolved sulphide of iron and reduces the electric resistance of the liquid.

Iron tanks are used as decomposition cells, and serve also as cathodes. When the tanks are rectangular, iron plates are suspended in the liquid to increase the cathode surface. Lead plates are used as anodes. Lead is not dissolved by the electrolyte in the presence of sulphur compounds; these latter also prevent the formation of large quantities of lead peroxide at the anode as it is reduced at once by the sulphur as soon as formed.

The tension required in each cell for the decomposition is stated to be 2 to 2½ volts, with a current of 3·7 to 4·6 ampères per square foot.

Borchers<sup>3</sup> found in the course of his investigations that the same quantity of antimony was separated from solutions of sulphantimonites and sulphantimonites for the same consumption of electrical energy, notwithstanding the difference in valency of antimony in the two classes of compounds. It would thus be unsuitable to bring the antimony into solution as sulphantimoniate, as sulphur would have to be added to the leaching liquor, and sodium sulphide or hydroxide to

<sup>1</sup> *Ber. Deutsch. Chem. Ges.*, vol. xviii., p. 1104; Classen, *Quint. chem. Anal. durch Elektrolyse*. Stuttgart, 1886.

<sup>2</sup> *Elektro-Metallurgie*, p. 148. Braunschweig, 1891..

<sup>3</sup> *Elektrometallurgie*, 1903, pp. 485, 486.

the electrolyte. The liberation of hydrogen gas along with metallic antimony at the cathode was confirmed, and at the anode the oxidation products of sodium sulphide, together with oxygen, sulphur, and antimony sulphide. Despite the investigations of Durkee,<sup>1</sup> Scheurer-Kestner,<sup>2</sup> and of Ost and Klapproth,<sup>3</sup> the reactions occurring during the electrolytic process are not yet quite clear.

The antimony is deposited as powder or as shining scales according to the current density. It falls partly to the bottom of the bath, and clings in part to the iron-plate electrode; from the latter it can be removed by means of a steel brush. After washing it is dried and then fused with addition of basic fluxes like soda or potash under a cover of antimony oxysulphide or of some sulphantimonite. In this way it is obtained pure.

The electrolyte, after being deprived of antimony, may be worked up for sodium thiosulphate (hyposulphite). This method, which is based on the use of insoluble electrodes, has not yet been established on a large scale.

Borchers<sup>4</sup> has also proposed a plant for the extraction of antimony. This is shown in Figs. 447 to 450. The trisulphide is dissolved in the conical vessel *a* (Figs. 447 and 448) by means of sodium sulphide solution. This is heated up to boiling by live steam from the pipe *b*, and the finely powdered ore added. After solution the whole is heated and agitated by a current of live steam; from time to time a blast of air from the steam blower *c*, attached to the pipe *b*, may be used for purposes of agitation. After the insoluble matter has settled, the liquor is drawn off through the pipe *f* into the collecting tank *g*. To get a constantly clear solution the vertical continuation of the pipe *f* in the solution bath operates in connection with a bell-shaped syphon *d*. This is a wide tube closed at the upper end, and capable of being raised or lowered by means of the chain and pulley, which hang over the open end of the pipe *f*. By moving this bell up or down, it is possible to run off the clear solution almost down to the level of the residues.

The solution is raised from the tank *g* through the pipe *h*, whence it flows along the gutter *i* into the holder *k*, and is distributed from there to the baths *l*. The spent liquor from the baths is drawn off through the gutter *m* to the storage tank *n*, and can be either sent back to the baths from this tank, or in case it is unfit for use it can be treated for sulphur or thiosulphate.

<sup>1</sup> *Zeit. für Elektro-chemie*, 1896, iii., 153.

<sup>2</sup> *Ibid.*, 1897, iv., p. 215.

<sup>3</sup> *Ibid.*, 1900, vii., p. 376.

<sup>4</sup> *Elektro-metallurgie*, 1896, 337; 1903, 487.

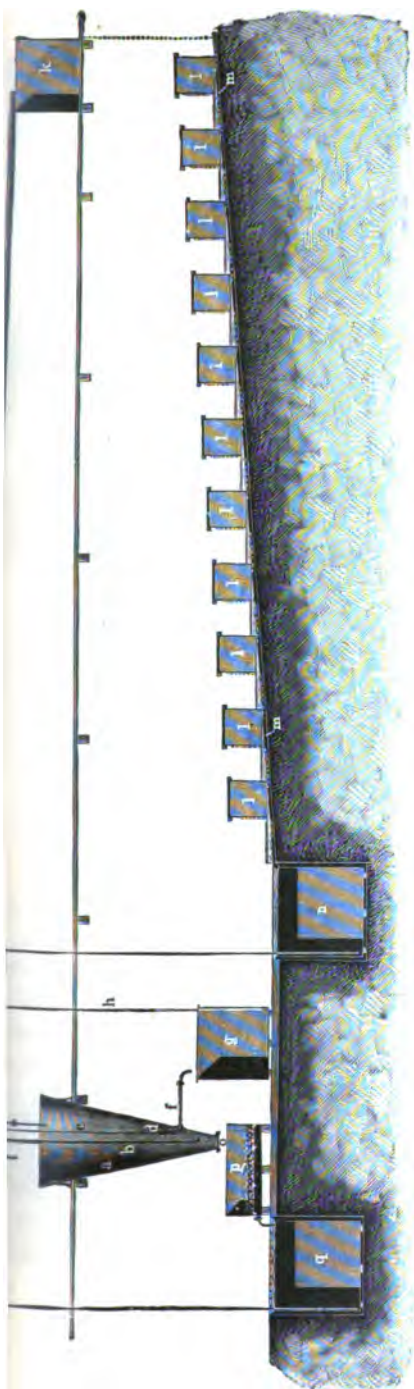


FIG. 447.

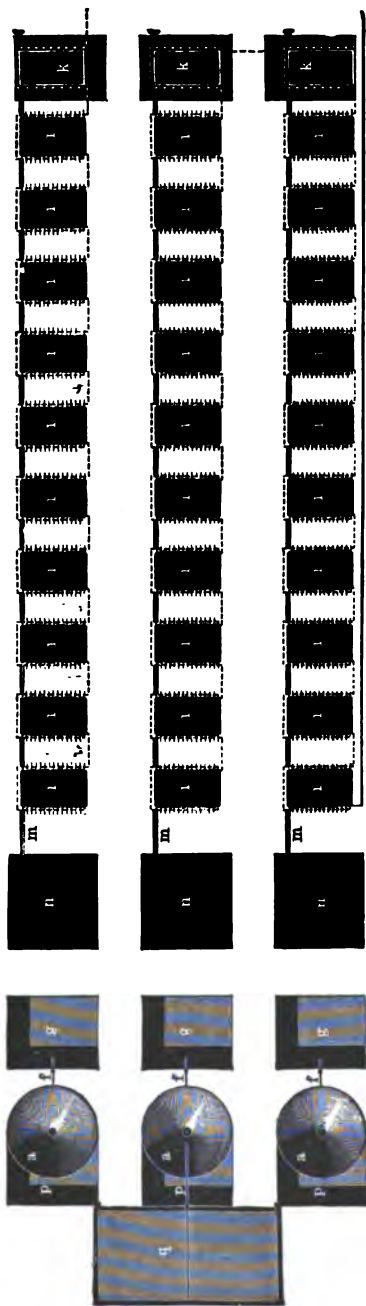


FIG. 448.

The residues from the first extraction are treated with fresh sodium sulphide solution and then boiled repeatedly with water. they are then allowed to escape through a hole in the bottom of the bath on to a filter *p*, where they are washed again with hot water. The wash-waters are collected in the holder *g*, and are used for washing other residues. The fresh sodium sulphide solution which is used after the first extraction is run into another solution tank and used to treat a fresh quantity of ore.

Figs. 447 and 448 are  $\frac{1}{250}$  of the natural size. Borchers thinks that with such a plant 6 to 8 cwts. of antimony could be extracted

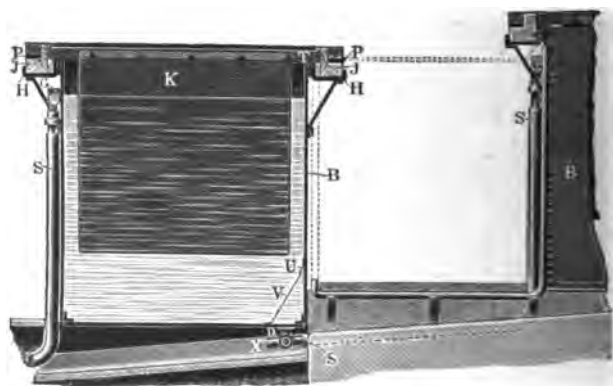


FIG. 449.

from ores containing less than 10 per cent. of the metal in 12 hours.

The arrangement of the electrolytic baths is seen (on a large scale) in Figs. 449 and 450. *A* are the anodes, *K* the cathodes. These are hung in iron baths. The cathodes are of sheet-iron and bolted on to the rails *T*, and rest directly upon the rim of the baths, so that the baths also are cathodes. The anodes are plates of lead suspended from iron rails which rest on the copper or iron strips forming the positive leads. These leads are isolated by resting on the wooden baulks *J*. The electrolyte is fed in at the bottom of the bath since it becomes less dense as the antimony is removed. This is effected by the three-way cock *D* under the bath, which also allows of the removal of liquor through the supporting tubes *X*. The electrolyte moves upwards in the bath and escapes at the overflow through the rubber pipes *S* into the next bath, the rubber serving to insulate the various baths from one another. An inclined plate *F* at

the bottom of the bath, and a plate *U* in the corresponding side of the bath, projecting over *V*, ensure the even distribution of the electrolyte by forming a channel the whole length of the electrodes, along which the liquid must flow. The sheet *V* also prevents particles of metal from being swept away from the bottom of the bath when the liquid is run off.

Koepp's method is to act on antimony sulphide with ferric

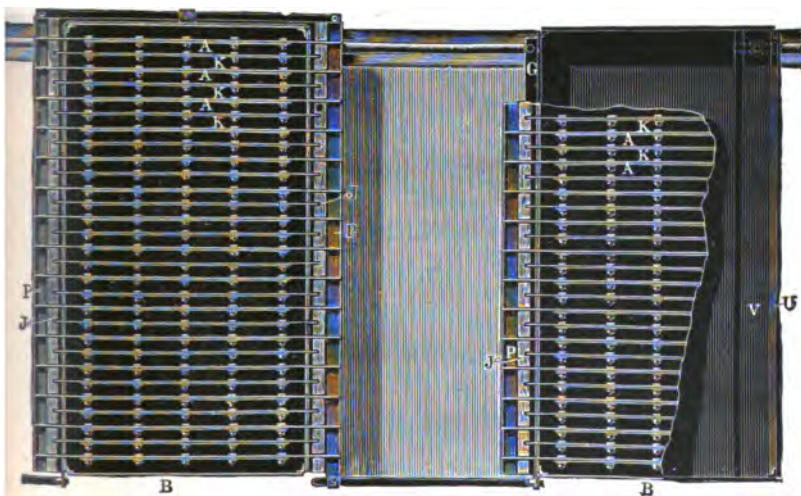
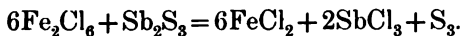


FIG. 450.

chloride with the result that ferrous chloride and antimony trichloride are formed and sulphur is separated, thus:—

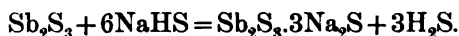


The solution is electrolysed at a temperature of 50° C. between lead plates. The antimony is deposited at the cathode and ferric chloride is formed at the anode. The current used is 3·7 ampères per square foot, but no information is given about the potential in the bath. It may be noted, however, that a practically useful metal is never obtained when chlorides are used as electrolytes.

Siemens and Halske<sup>1</sup> use as solvent either the sulphides, hydrosulphides or polysulphides of the alkalis. The finely ground ore is lixiviated with a solution of the sulphide, or hydrosulphide as the

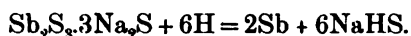
<sup>1</sup> German Patent, No. 67,973, June 29, 1892.

case may be, when the sulphide of antimony is brought into solution in the form of a double salt, *e.g.* with NaHS :—



The liquor is then led into the cathode division of a bath which is divided by diaphragms into series of anode and cathode divisions, the former being closed and gas-tight and containing insoluble anodes of carbon or platinum, and the latter being open and fitted with cathodes of copper or antimony plates.

The double salt is decomposed at the cathode, *viz* :—



In this way, in addition to the antimony, there is obtained a liquor which can be used again to dissolve more of the sulphide. Salt or some other alkaline chloride can be added to the solution in the anode cell, whereby chlorine will be liberated. If the lixiviation residues contain gold, silver, copper, mercury, bismuth, zinc, cobalt or nickel, they can be dissolved by means of the chlorine as chlorides and then precipitated by the sulphuretted hydrogen evolved during the lixiviation. If there are none of these metals to be treated in this way the chlorine can be used for other purposes, *e.g.* bleaching.

No practical application appears to have been made so far of this process.

Another process of Siemens<sup>1</sup> is to convert antimony sulphide into a double salt by treatment with sulph-hydrate of calcium, barium, strontium or magnesium, and to electrolyse the solution of this salt without using diaphragms. The hydrogen liberated at the cathode combines with the sulphur of the antimony sulphide, antimony is deposited and the sulph-hydrates of the other metals are formed, which latter are converted into disulphides by the oxygen developed in the reaction. Treatment of these disulphides with carbon dioxide causes the precipitation of carbonates of calcium, barium, strontium, and magnesium, and of elemental sulphur, and hydrogen sulphide is evolved. The mixture of the carbonates and sulphur when heated in absence of air yields sulphur, carbon dioxide and the caustic alkaline earths. The carbon dioxide may be used to decompose disulphide solutions, and the basic oxides and hydrogen sulphide to produce fresh quantities of the sulph-hydrate solution. This process has not come into use.

<sup>1</sup> English Patent, April 1, 1896, No. 7,123.



According to Izart,<sup>1</sup> experiments have been made in France at Cassagnes, on the electrolysis of the solution obtained by lixiviating antimony ores with sodium sulphide. The method is as follows:—The antimony solution in the cathode chambers is separated by diaphragms from the solution in the anode chambers, which consists of a 17 per cent. solution of caustic soda, to which enough ammonium chloride is added to bring up its density to that of the antimony solution. On electrolysis at a tension of 1·8 volts and a current density of 68 ampères per square yard, the yield was 76 per cent. The yield per kilowatt-hour was at first 1·21 lbs. of antimony; afterwards 1·36 lbs.

Impure antimony which contains gold was for a short time worked up for the extraction of both metals at Lixa near Oporto in Portugal:<sup>2</sup> the process was, however, given up on account of the high working cost. Plates of the impure antimony were used as anodes, the electrolyte being a solution of antimony trichloride. The latter was made by dissolving the trichloride in a concentrated solution of salt, potassium chloride or ammonium chloride strongly acidified with hydrochloric acid. When the current was passed the anodes slowly dissolved, the antimony being deposited on the cathode while the gold in fine powder fell to the bottom of the cell. The material of which the cathode was made is not stated. In spite of the fact that soluble anodes were used, the method proved to be too costly.

<sup>1</sup> *L'Electricien*, 1902, xxii., I., p. 307; II., p. 33. *Journ. Soc. Chem. Ind.*, xxi., p. 1237, October 15, 1902.

<sup>2</sup> J. H. Vogel, *Zeitschr. für Angew. Chem.*, 1891, p. 327, and Sanderson, German Patent, No. 54,219, February 26, 1890.

## ARSENIC

### PHYSICAL PROPERTIES

THIS metal possesses a steel grey colour, and shows a brilliant lustre when freshly broken; it is known in both the crystalline and amorphous conditions. The crystalline form belongs to the hexagonal system, and is isomorphous with tellurium and antimony, while the amorphous form is a dark grey powder which changes into the crystalline modification when heated to  $370^{\circ}\text{C}$ .

The crystalline form can be obtained by collecting the vapour of the metal in a receiver which is only a few degrees colder than the vapour itself; if the difference of temperature be great the amorphous form is deposited. It is also deposited in the amorphous condition when the vapour of arsenic mixed with other gases (e.g. hydrogen or oxides of carbon) is cooled.

The crystalline form is brittle and somewhat hard, but the cast metal flattens slightly under the hammer, although it is easily broken.

The specific gravity of the crystalline variety is 5.727 at  $14^{\circ}\text{C}$  and its specific heat 0.083 (Wüllner and Bettendorf). The specific gravity of the amorphous variety is 4.71.

Arsenic can be fused at a dark red heat if contained in a sealed glass tube under pressure.<sup>1</sup>

According to Conechy arsenic volatilises at a temperature of  $449^{\circ}$ — $450^{\circ}\text{C}$ . as a citron yellow vapour which has a strong smell of garlic; it is doubtful if the smell is due to the metal or to some low oxidation product. The vapour, as already pointed out, may be condensed either as crystals or as a dark grey amorphous powder.

<sup>1</sup> Landolt and Mallet, *Dingler*, vol. civ. p. 575.

THE CHEMICAL PROPERTIES OF ARSENIC AND ITS COMPOUNDS  
THAT ARE OF IMPORTANCE IN ITS EXTRACTION

Arsenic does not change in dry air at ordinary temperatures, but in damp air it loses its colour and brilliancy and changes slowly into arsenious oxide. When heated in the air it burns with a bluish-white flame, forming a copious white cloud of arsenious oxide.

Nitric acid oxidises it to arsenious oxide. Aqua regia dissolves it easily, forming a mixture of arsenious and arsenic oxides. Hot concentrated sulphuric acid dissolves it with liberation of sulphur dioxide; the dilute acid does not attack it. Hydrochloric acid attacks it only in presence of air, and then but feebly, with formation of arsenious chloride. Chlorine combines eagerly with it in the cold, forming arsenious chloride. When heated with sulphur it forms sulphide of arsenic.

If arsenic be heated with nitre or chlorate of potassium, an active oxidation of the metal takes place, and potassium arseniate is produced.

## OXYGEN COMPOUNDS OF ARSENIC

Arsenic forms two compounds with oxygen, arsenious oxides and arsenic oxide; both of these are acid-forming bodies, and have a much wider technical application than the metal has.

*Arsenious Oxide,  $\text{As}_2\text{O}_3$ , or  $\text{As}_4\text{O}_6$* 

This is also known as arsenious anhydride, arsenic trioxide and white arsenic. It is white, and occurs in both the crystalline and amorphous states.

The crystalline form is dimorphous; it crystallises in the cubic and in the rhombic systems. Octahedra are obtained by cooling a hot aqueous solution of the oxide; a solution in hydrochloric acid gives better results. Rhombic prisms crystallise from a saturated solution in caustic potash. The latter form can also be obtained by heating arsenious acids in closed vessels to a temperature of  $300^\circ \text{C}$ .; when left at rest for a long time it slowly changes into the amorphous form.

Amorphous arsenious acid, also known as "arsenic glass," is prepared by subliming the crystalline variety at a high temperature. It is a white transparent mass, which, when left at rest for a long time, changes into the crystalline form, loses its transparency, and assumes a porcelain-like appearance. When arsenious oxide is heated in a closed tube placed in a vertical position, the lower end being

at a temperature of  $400^{\circ}\text{C}$ . and the upper at  $200^{\circ}\text{C}$ ., the arsenious oxide in the lower part of the tube will be found in the amorphous condition, that in the middle in rhombic prisms, and that at the upper end in octahedra.

The amorphous variety dissolves readily in water and alcohol. The crystalline varieties, however, are only soluble with difficulty in these liquids.

Amorphous arsenious oxide fuses when heated at the ordinary pressure of the atmosphere; the crystalline variety, on the other hand, only fuses under pressure, and solidifies again in the amorphous form.

Arsenious oxide volatilises when heated. The temperature at which it volatilises is given by Wurtz at  $200^{\circ}$ , by Watt at  $218^{\circ}$ , by Wormley at  $190^{\circ}\text{C}$ . When a solution of the oxide is evaporated, the oxide is said to begin to volatilise with its solvent between  $100^{\circ}$ — $150^{\circ}\text{C}$ . Arsenious oxide is reduced when heated with charcoal; the metal volatilises and may be obtained as a brilliant black sublimate.

Arsenious oxide is a powerful reducing agent, and is extensively used on this account as a decoloriser in glass-making, in the manufacture of copper colours, and for the manufacture of yellow arsenic glass.

Arsenious oxide does not combine directly with oxygen, but by the use of strong oxidising agents, such as aqua regia, chlorine, nitre and nitric acid, it can be converted into the higher oxide of arsenic, arsenic oxide. The principal use of arsenious oxide is in preparing arsenic oxide, which is largely employed in the manufacture of aniline dyes.

#### *Arsenic Oxide or Arsenic Anhydride, $\text{As}_2\text{O}_5$*

This exists both as the anhydride and in combination with water as the corresponding acid. As is the case with the corresponding oxide of phosphorus, arsenic oxide forms three different acids, arsenic acid  $\text{H}_3\text{AsO}_4$ , pyroarsenic acid,  $\text{H}_4\text{As}_2\text{O}_7$ , and metarsenic acid,  $\text{HAsO}_3$ . These and their salts are isomorphous with the corresponding acids and salts of phosphorus. The pyro- and meta-acids of arsenic, however, are not stable in aqueous solutions as the corresponding acids of phosphorus are; in contact with water they are converted into the ordinary ortho-acid.

The anhydride is a white substance which is only slightly soluble in water, but combines with it if the two are left in contact for a time, forming the acid, which is soluble. At a red heat the anhydride fuses and decomposes into arsenious oxide and oxygen.

Arsenic acid of commerce,  $\text{H}_3\text{AsO}_4$ , is a thick liquid, which, on being heated to the temperature of  $180^\circ \text{C}$ ., changes into hard, glistening crystals of the pyro-acid,  $\text{H}_4\text{As}_2\text{O}_7$ , with elimination of water. At a higher temperature,  $200^\circ \text{C}$ ., more water is eliminated, and the meta-acid  $\text{HAsO}_3$  is obtained, a white glistening body resembling mother-of-pearl.

#### SULPHIDES OF ARSENIC

Arsenic forms three sulphides, arsenic disulphide,  $\text{As}_2\text{S}_2$ , arsenic trisulphide,  $\text{As}_2\text{S}_3$ , and arsenic pentasulphide,  $\text{As}_2\text{S}_5$ .

The *disulphide* occurs native as the mineral realgar. A substance of similar composition is manufactured under the name red arsenic glass. This latter substance is used in the preparation of the so-called "Indian fire," and also in tanning, where it is combined with lime for the removal of hair from the hides. It was formerly widely used as a pigment, but latterly has largely gone out of use.

The *trisulphide* is found in nature as the mineral orpiment (*auripigmentum*). It can be prepared artificially by passing sulphuretted hydrogen through an acidified solution of arsenious oxide. If this sulphide be heated out of contact with air it fuses to a yellowish-red liquid which volatilises without decomposition at the temperature of  $700^\circ \text{C}$ . If heated in the air, however, it burns with the production of arsenious oxide and sulphur dioxide. It is insoluble in strong hydrochloric acid, while the sulphides of antimony and tin are soluble. It is soluble in solutions of the caustic alkalis and in solutions of the alkaline carbonates, forming an arsenite and a sulpharsenite of the alkali metal, *e.g.* :—



Arsenic trisulphide is again precipitated from this solution on adding an acid.

This sulphide of arsenic was formerly highly esteemed as a pigment in oil painting, but has of late years been replaced by chrome yellow and picric acid. It is chiefly used now in the same way as realgar.

*Arsenic pentasulphide* is prepared either by fusing together the trisulphide and sulphur, or by treating sodium sulpharseniate,  $\text{Na}_3\text{AsS}_4$ , with an acid. The latter salt is obtained by acting on the trisulphide with polysulphide of sodium.

#### HYDRIDES OF ARSENIC

There are two of these compounds, gaseous arseniuretted hydrogen  $\text{AsH}_3$ , and solid arseniuretted hydrogen,  $\text{As}_4\text{H}_2$ . The former, which



is extremely poisonous, is prepared by generating hydrogen in a solution which contains arsenic; the latter is a brown solid body, and is prepared by acting on pure sodium arsenide with water.

#### CHLORIDE OF ARSENIC

is produced when powdered arsenic is burned in chlorine gas, or by distilling arsenious oxide with hydrochloric acid. It is an oily colourless liquid which, when exposed to the air, evaporates in white, highly poisonous vapours.

#### COMBINATIONS OF ARSENIC WITH OTHER METALS

Arsenic combines with certain metals forming bodies known as speiss. These only faintly resemble alloys, being much more closely allied to the compounds of metals with the non-metallic elements.<sup>1</sup>

#### ORES OF ARSENIC

Arsenic and its technically important compounds are extracted from nickel and cobalt ores as well as from specific ores of arsenic. Among the latter, *native arsenic*, *mispickel*, and *leucopyrite* are the most important. The other arsenic minerals, *arsenic bloom*, *realgar* and *orpiment*, occur but seldom, and do not form the subject of special processes for the preparation of arsenical products, but are worked up with other ores of arsenic.

#### *Native Arsenic*

*Native Arsenic*, also known as *flaky arsenic*, usually contains small quantities of iron, cobalt, nickel, antimony, silver and frequently also gold. It usually occurs in association with silver, lead, cobalt and nickel ores, and is found in the Erzgebirge (Freiberg, Annaberg, Marienberg, Schneeberg), in the Harz (St. Andreasberg), in Hungary (Kapnik, Orawitz), Norway (Kongsberg), France (St. Marie aux Mines, Allemont), Italy (Mte. Corna near Darden, Valtellina), Cornwall, Siberia (Zmeoff), Chili (Chanarcillo), Mexico (San Augustin, Hidalgo) and New Zealand (Kapanga Mine).

#### *Mispickel*,

$\text{FeS}_2 + \text{FeAs}_2$ , *arsenopyrite*, or *arsenical pyrites*, contains arsenic 46.1 per cent., sulphur, 19.6 per cent., and iron, 34.3 per cent. The

<sup>1</sup> Schnabel, *Allgem. Hüttenkunde*, p. 10.

iron is sometimes replaced to the extent of from 6 to 9 per cent. by cobalt, in which case it constitutes a cobalt ore. It also contains sometimes small quantities of gold and silver. It is the most widely distributed ore of arsenic, occurring in the Erzgebirge, Silesia (at Reichenstein), Hungary, Styria, England (Cornwall and Devon), Sweden, France (Puy de Dome and Haute Loire), Portugal (Oliveira in the Aveiro district), Spain (Bustar viejo, Corunna, Ferrol), Turkey (Jevikoï, Aidin province and Asia Minor), Canada (Deloro, Hastings Co., Ontario), United States (Seattle, Washington), and in Australia. It is accompanied by silver, nickel, cobalt, tin, lead and copper ores as well as by pyrites.

### *Arsenide of iron*

occurs massive as *löllingite* and crystallised as *leucopyrite*. *Löllingite* ( $\text{Fe}_2\text{As}_3$ ) contains 66·8 per cent. arsenic, while *leucopyrite* ( $\text{FeAs}_2$ ) contains 72·84 per cent. These frequently contain small quantities of gold, as at Ribas in Spain, and at Reichenstein in Silesia. At the former place the *leucopyrite*, according to Güttler, contains from 14 to 16 dw. of gold per ton.

This mineral occurs less copiously than *mispickel*, and is found at Silesia, Reichenstein, Bohemia, Styria, Schladming, Carinthia (*Lölling*, near *Hüstenberg*). It is usually found in association with the same ores as *mispickel*.

The rare minerals—*arsenic bloom*, *arsenite*, or *arsenolite*,  $\text{As}_2\text{O}_3$ , *realgar*,  $\text{As}_2\text{S}_2$ , and *orpiment*,  $\text{As}_2\text{S}_3$ —are of no importance as sources of arsenic. *Realgar* is found in Macedonia, *Aserbreidschan*, Persia; *orpiment*, at *Allkhar* near *Rozdan*, Macedonia.

Among the arsenical cobalt and nickel ores must be mentioned *cobalt glance*, *tin-white cobalt* or *smaltine*, *skutterudite*, *white arsenical nickel*, *red arsenical nickel*.

In addition to the above sources of arsenical products, ores of tin, silver, lead and copper, which contain *mispickel* or *leucopyrite*, produce considerable quantities as by-products.

## THE METALLURGICAL EXTRACTION OF ARSENIC AND ITS COMPOUNDS

In addition to metallic arsenic, which has comparatively small technical importance, arsenious oxide, sulphide of arsenic, and mixtures of these are prepared in metallurgical works. The quantity of these arsenic compounds used in the arts is very considerable.

Dry methods are used for the working of ores and metallurgical products, but wet methods have been proposed for the recovery of

arsenical compounds from residues from the manufacture of the aniline colours. The electrolytic method has been proposed for the extraction of arsenic from its sulphide, but so far has not been put into practice.

We have therefore to distinguish between:—

I. The extraction of arsenical compounds from ores and metallurgical products.

II. Methods proposed for the recovery of arsenical compounds from coal-tar colour residues.

## I. THE EXTRACTION OF ARSENICAL COMPOUNDS FROM ORES AND METALLURGICAL PRODUCTS

Here we must further differentiate into:—

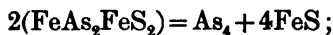
1. The extraction of arsenic.
2. The extraction of arsenious acid.
3. The preparation of vitreous realgar.
4. The preparation of vitreous orpiment.

### 1. THE EXTRACTION OF ARSENIC

#### A. *Extraction by the Dry Method*

Almost the only dry method of extracting arsenic is that of heating mispickel or leucopyrite in the absence of air. Formerly another method was employed, viz., by the reduction of arsenious acid by means of carbon. This method is, however, now abandoned, because a very large proportion of the arsenic prepared by it was obtained in the amorphous condition.

When mispickel is distilled the arsenic is driven off and can be collected. The following equation shows theoretically the chemical change which takes place:—



but in actual working a very considerable quantity of the arsenic, amounting in some cases to a half, remains behind in the residue.

Leucopyrite, when distilled, parts with a portion of its arsenic, and leaves behind a lower arsenide of iron as shown by this equation:—



In practice, however, the residue is richer in arsenic than it should be theoretically.



To prevent waste of the arsenic in the residues from the above processes, they are roasted in a reverberatory furnace, and the arsenious oxide which is formed, is collected.

As the arsenic is only wanted in the crystalline form, the sublimation must be conducted with the greatest care and the receivers must be maintained at the correct temperature.

The formation of more or less of the amorphous pulverulent arsenic cannot in any case be prevented; and it is used for the preparation of arsenical compounds.

The distillation is performed in pot furnaces built of fire-clay. Tubes or pots are arranged in two rows, one on each long side of a fireplace in a galley furnace. Where pots are used, several rows can be arranged one above the other. To the front of the pots, cylindrical receivers of fire-clay are attached. These are provided on their front side with doors of sheet iron, by opening which the progress of the sublimation can be observed towards the end of the process. The joint between the sublimation vessel and the receiver must be properly luted, and the door on the receiver must be made tight with clay. In order to prevent loss by volatilisation during the working, the tubes themselves are glazed externally. They are 5 to 7 inches in diameter and 2 feet 4 inches long. The charge in each tube is several pounds of mispickel. Sheet iron rolled into a spiral is placed in the mouth of each tube so that it projects 4 inches into the receiver and 4 inches into the tube. This assists the formation of crystals of arsenic in the shape of glistening grey scales.

After the tubes or jars are charged, the spiral of sheet iron is placed in position, and the fire started: the receivers are not put on until arsenic vapour begins to appear. The process is complete when no more arsenic vapour is seen on opening the doors of the receiver. When mispickel is treated in the way described above, sulphide of arsenic is volatilised at the beginning of the process and collects in the receiver (Freiberg). The addition of potash or caustic lime prevents the sublimation of sulphide. The time required for the process varies, according to the amount of arsenic in the ore, from 8 to 12 hours, where charges of several pounds per tube are used. After the completion of the process the receivers are taken away, and the sublimation residues are removed.

Crystalline arsenic collects on the iron spiral in the mouth of the tube, while the larger portion of that which collects in the cooler parts of the receiver, is amorphous. The spirals are cautiously unrolled to remove the scales of arsenic which have been deposited. These scales possess a particularly bright lustre, and are fit for sale without

further treatment; they lose their brilliancy after a very short time, in consequence of the formation of a thin film of arsenic suboxide, but according to Boettger, this film can be easily removed by a boiling hot solution of potassium bichromate to which a little sulphuric acid has been added.

At Freiberg, ores containing,<sup>1</sup> 76 per cent. of mispickel (i.e. 35 per cent. of arsenic) are worked in galley furnaces, in which there are 26 tubes in two rows on each side, 6 in the upper and 7 in the lower row. The charge of ore for the whole furnace is 7 cwt. and the extraction requires 10 or 12 hours. The product is 165 lbs. of arsenic from the spiral of sheet iron, and 27 lbs. of sulphide of arsenic out of the receivers. The residues, which are argentiferous, retain 3 per cent. of arsenic. They are added to a furnace charge in smelting for silver-lead in order to extract their silver. The sulphide which collects in the receivers is used for the preparation of vitreous realgar.

At Reichenstein,<sup>2</sup> in Silesia, arsenic is extracted from mispickel. The furnace formerly used contained 26 glazed tubes, each 2 feet to 2 feet 6 inches long and about 5 inches wide, and the charge was 5 cwt. of mispickel in the form of slimes. The product consisted of 90 per cent. of crystalline, and 10 per cent. of amorphous arsenic: the residues which retained one-third of the arsenic originally present in the ore, were worked up for the production of arsenious acid.

At Ribas<sup>3</sup> in Spain, arsenic used formerly to be extracted. There were 22 tubes per furnace, each 2 feet 4 inches long, and about 7 inches in diameter: 8 to 10 cwt. were charged at a time, and the process lasted 9 hours. In this time 200 pieces of peat and 2·7 to 3·9 cubic yards of coal were consumed. The arsenic obtained was used in the manufacture of shot.

Efforts have been made recently to prepare arsenic from mispickel by heating it in an electric furnace in an atmosphere of nitrogen,<sup>4</sup> whereby the arsenic is volatilised and the sulphide of iron melts and is removed as a matte from the furnace. The arsenic vapour and the nitrogen are conveyed by a small fan into condensers, where the arsenic collects as a powder and the nitrogen is sent back again into the furnace. To prevent over-heating of the condensers, two series of them are arranged for alternate use. No details of working results of the process are known.

<sup>1</sup> *Preuss. Zeitschr.*, vol. xviii., p. 189.

<sup>2</sup> Kerl, *Metallurgy*, p. 506.

<sup>3</sup> *Berg- und Hütten-Ztg.*, 1853, p. 764.

<sup>4</sup> *The Min. Ind.*, 1902, p. 42.

### B. *The Electro-Metallurgical Extraction of Arsenic*

Siemens and Halske<sup>1</sup> have proposed this method for the extraction of arsenic from those ores and intermediate products which contain the sulphide. By treatment of the ores with sulphides, hydro-sulphides or polysulphides of the alkali metals, the arsenic is brought into solution as a double salt, and the latter is subjected to electrolysis. Sodium hydro-sulphide gives a solution according to the equation:—



Similar soluble salts are produced by the hydro-sulphides of potassium and ammonium. The arsenic is separated from these solutions in the manner described for antimony on page 596. The following equation shows the change which takes place when the arsenic is precipitated by the current:—



and similarly for the double salts formed with potassium and ammonium respectively. In the anode division of the bath alkaline chlorides are decomposed, the chlorine evolved being utilised in order to bring into solution as chlorides the metals contained in the ore residues, or, if there are none present, for the preparation of bleaching powder. There has been so far no application of these methods, and the prospect of their introduction is very small, because the real ores of arsenic are leucopyrite and mispickel, from which arsenic cannot be directly extracted as sulphide.

In another process proposed by A. Siemens<sup>2</sup> the sulphide of arsenic is brought into solution by sulph-hydrates of calcium, strontium, barium or magnesium, and the solution electrolysed without using diaphragms. The hydrogen separated at the cathode combines with the sulphur of the sulphide forming sulph-hydrates of the basic metals, which are oxidised to disulphides by the oxygen developed in the process. The sulphides on treatment with carbon dioxide are decomposed with precipitation of sulphur and the carbonates of calcium, strontium, barium and magnesium, and the liberation of hydrogen sulphide. The precipitate on heating out of contact with air yields carbon dioxide, sulphur and the oxides of the metals, and of the various products the carbon dioxide may be used for the decomposition of disulphide solution, the metallic oxides and the hydrogen sulphide for the preparation of fresh sulph-hydrate solution. This method also has not come into use.

<sup>1</sup> German Patent, No. 67,973, June 29, 1892.

<sup>2</sup> English Patent, No. 7,123, April 1, 1896.

## 2. THE MANUFACTURE OF ARSENIUS OXIDE

Arsenious oxide is produced by the roasting of special ores of arsenic or of those ores of gold, silver, nickel, cobalt, lead, copper and tin, which contain arsenic.

The special ores of arsenic are mispickel, leucopyrite and native arsenic; the others, particularly the ores of tin, copper and gold, usually contain large quantities of these arsenic compounds, especially mispickel.

By far the largest quantity of arsenious oxide produced at the present time comes from Cornwall and Devon, where it is extracted from mispickel, either pure, or mixed with ores of copper and tin. The following are the principal mines:—Botallack, Levant, East Pool, South Crofty, Tin-croft, Wheal Agar, Callington United, Danescombe and Drakewells in Cornwall, and Devon Great Consols and Gawton in Devonshire.

The process adopted for the extraction of arsenious oxide is to drive off the arsenic in the ore as arsenious oxide by roasting, and to collect the latter in chambers and flues; in most cases the flue dust contains impurities and needs to be purified by sublimation. Sublimed arsenious oxide is either crystalline, or in the form of white powder: the latter form, sometimes obtained by grinding the crystals, is most frequently met with in trade; some however is found in the form of lumps, the so-called *arsenic glass*, *vitreous arsenic* or *white glass*. It is prepared by subjecting the purified arsenious oxide to a further sublimation at a higher temperature.

We must therefore distinguish between:—

- A. The extraction of crude arsenious oxide.
- B. The purification of crude arsenious oxide.
- C. The preparation of vitreous arsenic.

### A. The Manufacture of Crude Arsenious Oxide

Arsenical pyrites, mispickel and native arsenic, either alone or mixed with other ores, are the special sources of arsenious oxide. The changes which occur when these are roasted are the following:—

*Leucopyrite* ( $\text{FeAs}_2$ ). At a dull red heat, arsenic vapour is given off, being followed by arsenious oxide as the temperature rises. The iron is nearly all converted into ferric oxide, but a small proportion is converted into ferric arseniate.

*Mispickel* ( $\text{FeS}_2 + \text{FeAs}_2$ ). Below red heat it evolves arsenic sulphide vapour. At higher temperatures it is converted into a mixture

of ferric oxide, ferric sulphate and ferric arseniate, sulphurous acid and arsenious oxide being at the same time liberated.

*Native arsenic* is changed into arsenious oxide.

The operation of roasting takes place either in muffle furnaces or in reverberatory furnaces. In the former the fuel consumption is higher, but on the other hand neither ore dust nor small particles of coal nor soot get mixed with the arsenious oxide. The latter would be a serious matter, as during the sublimation the arsenious oxide would be reduced by the carbonaceous matter to metallic arsenic.

In reverberatory furnaces this difficulty is best avoided by the use of gas as fuel.

The furnaces must be connected to condensing chambers and flues, suitably constructed for the recovery of the arsenious oxide.

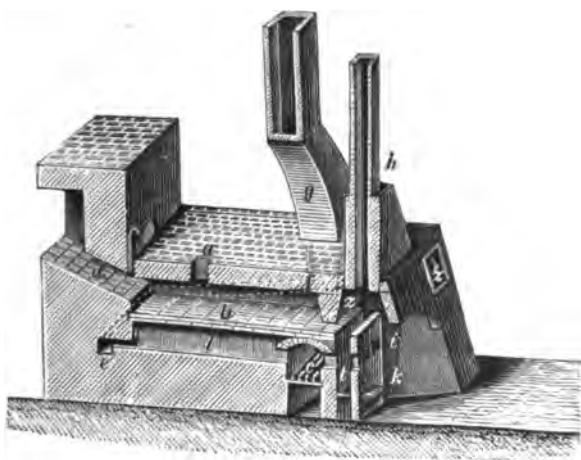


FIG. 451.

The flues or chambers are best built on a level for convenience of emptying. With muffle furnaces it is important to have sufficient cooling in the flues in order to maintain the draught and to prevent the formation of large crystals of arsenious oxide. The best material to use for the flues is sheet lead, over which water can be allowed to trickle in case of need. The so-called "poison-towers," which were tower-shaped erections with flues, one above the other, have gone out of use on account of the excessive draught and the difficulty of cleaning them out.

The construction of a muffle furnace such as was formerly in use at Reichenstein in Silesia is shown in Fig. 451, in which *b* is the muffle,

of which the bed is 11 feet 3 inches long and 7 feet 2 inches broad : *c* is the fire-place : the fire gases travel through 5 channels *l* below the bed towards the cross flue *e*, and through them into the flues *f*, one on each side of the furnace and on to the forked chimney *g*. The arsenious oxide liberated in the muffle passes along the flue *d* into a system of condensing flues not shown in the figure ; the air required to oxidise the charge enters at the opening *i*. The small chimney *k* serves to carry off the fumes which escape at the working door *z*. The residues in the muffle were drawn into the chamber *t* after the removal of the slide *h*, and *a* is a hole in the roof through which the ore is introduced on to the bed.

At St. Andreasberg in the Harz, cast-iron muffles, 7 feet 6 inches long, 1 foot 7 inches wide, and 1 foot 2 inches high, were formerly employed.

At Freiberg, reverberatory furnaces with a single bed and two working doors on each side are used ; they are heated by producer gas made from gas coke : the beds are 15 feet long and 10 feet 10 inches wide.

In Cornwall and Devonshire the arsenical ores are roasted in hand-worked long-bedded reverberatory furnaces, or in Brunton's rotary calciner, or Oxland's rotating cylinder furnace.

The long-bedded reverberatory furnace has working doors on one only of the long sides, the other long side being also the long side of a contiguous furnace. These double furnaces measure over all 24 feet long and 16 feet wide, and the dividing wall is 1 foot 6 inches thick. The inside measurements of a single furnace are :—length 20 feet, width 6 feet 3 inches, and the maximum height of the roof above the bed 1 foot 4 inches. The fire-place for each furnace is 4 feet long and 2 feet wide, and the top of the fire-bridge is 9 inches above the surface of the bed. There are 5 or sometimes 6 working doors and the ore is introduced through a hopper at the end farthest from the fire and spread towards the bridge.

Brunton's calciner is arranged as shown in Figs. 452 and 453. *a* is the bed fixed to a vertical shaft, *b* is the fire-place, *c* is the hopper through which the ore is introduced into the furnace. A fixed rake *f*, which stirs up the ore as the bed *a* revolves, causes the ore to travel gradually from the centre to the circumference when it escapes through the shoot *g* into one of the chambers *h, h*, according to the position of the slide *z*. The flue connecting the furnace with the chimney *v* is not shown in the figure. The diameter of the bed is from 12 to 16 feet, and it makes from 5 to 10 revolutions per minute.

The Oxland furnace is shown in Figs. 390 and 391 on page 489. The length of the inclined cylinder is 23 to 30 feet, and it is lined with firebrick and provided with longitudinal ribs; its diameter is about 5 feet. The power required for one furnace is about 2 to 3

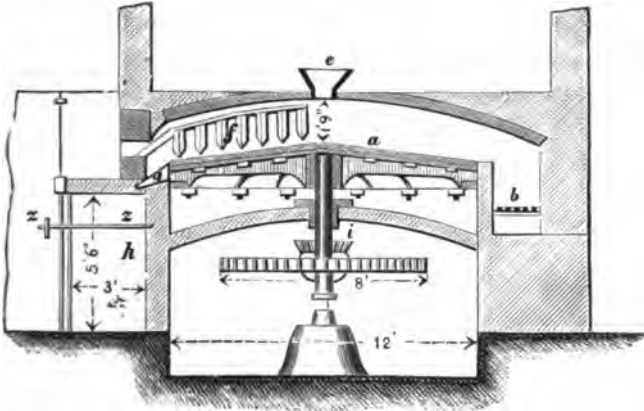


FIG. 452.

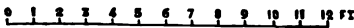
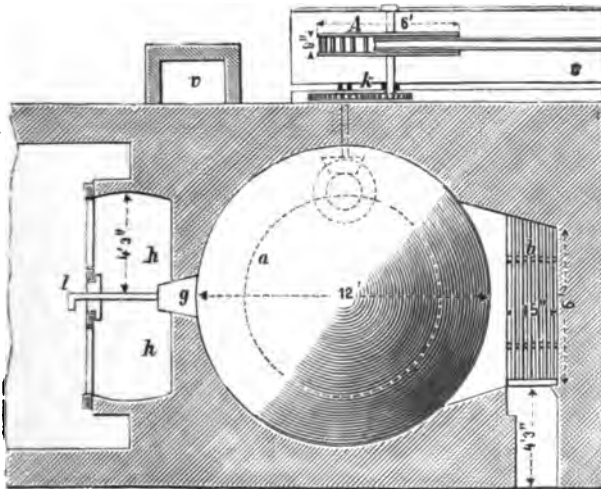


FIG. 453.

horse power. A full description of this furnace will be found on page 489. This pattern of furnace requires less fuel and labour than the long-bedded furnace or Brunton's calciner, but the cost of repairs is greater and it is more difficult to maintain in it an even

temperature and a regular draught. In consequence of the strong draught fine particles of ore are drawn into the flues and deposited with the arsenious oxide.

At Deloro, in Canada,<sup>1</sup> mispickel which contained gold was formerly worked. The ore contained 42 per cent. of arsenic and 20 per cent. of sulphur. The furnace used consisted of two cylinders of the Oxland type one above the other. Instead of the longitudinal rows of projecting ribs, there were four walls extending from the axis of the cylinder to the circumference, thus dividing it into four entirely separate portions. In the upper half of the furnace the ore remained in one of these four portions of the cylinder; but in the lower half of the cylinder the division walls were provided with slits so that the ore could fall from one of the four divisions into the next to it, thus coming into intimate contact with the air. The air was drawn out by an exhauster placed near the chimney.

The length of the upper cylinder was 29 feet 6 inches and its diameter 5 feet 6 inches, and it was connected by a tube with the lower cylinder 59 feet long and 6 feet 6 inches diameter, and was worked by natural draught. It contained division walls, like the upper cylinder, extending from the lower end to a distance of 4 feet from the upper end, but for the remaining distance it was provided with ribs; these, however, were not placed longitudinally but spirally. The greater portion of the arsenic was driven off in the upper cylinder. The arsenious oxide which was collected in the condensing chambers was re-sublimed in reverberatory furnaces.

At present the mispickel used for the preparation of oxide of arsenic, is first treated for gold by amalgamation and then by the bromo-cyanogen process.<sup>2</sup> After this treatment it contained 30 per cent. of arsenic and 16 per cent. of sulphur. It is roasted in the way described above, and the vapours are led into a chamber 100 feet long, where portions of the charge carried over are collected and returned to the furnace, and then into a zig-zag condenser 12 feet wide, in which the arsenious oxide is condensed. This oxide contains 85 per cent. of  $\text{As}_2\text{O}_3$  and 2 to 4 per cent. of sulphur; it is resublimed in reverberatory furnaces. The residue from the upper furnace only contained 0.36 per cent. of arsenic and in addition 43.23 of silica, 44.60 of ferric oxide, and 5.04 of sulphur.

All the furnaces are connected with a set of flues or chambers in which the volatilised arsenious oxide is condensed as flue dust. These are built of either masonry or sheet lead. It was proposed

<sup>1</sup> *The Min. Ind.*, 1893, p. 35.

<sup>2</sup> *The Min. Ind.*, 1903, p. 47.



for pure ores to use chambers built of sheet iron suitably protected from rusting.<sup>1</sup>

Pure arsenious oxide in the form of a fine powder is said to be deposited in these chambers as the result of roasting pure ores.

Fig. 454 shows the ground plan of a condensing flue for arsenious acid; *v* is the furnace, *k* is the flue, zig-zag in plan, and opening into the dust chamber *z*. The gases on leaving the chamber *z*, pass through a second chamber *y* into the chimney *E*. Most of the arsenious oxide is deposited at the bends of the flue.

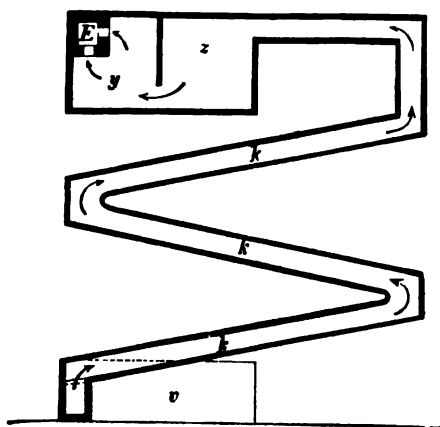


FIG. 454.

The flue walls near the furnace are built of masonry, but after a certain distance from the furnace sheet lead is the best material.

The construction of the tower-condenser or "poison-tower," which was formerly used, is shown in Fig. 455. Chambers were built alongside each other in sets, one set above the other, and the stream of furnace gases, after passing through one set of chambers, went on to the set next above, till at the end it entered the chimney *z* placed on the top.

This arrangement is not efficacious for cooling the gases, it is expensive in construction, and is difficult to clean. This latter objection is of importance on account of the poisonous nature of the arsenious oxide: it is therefore no longer used.

In Cornwall and Devonshire the arsenic is condensed in zig-zag flues built of masonry, and connected with the furnace by straight flues 100 to 200 feet in length. They are 5 feet to 5 feet 6 inches high, 3 feet to 3 feet 6 inches wide, and in some cases more than

<sup>1</sup> *Ibid.*, p. 35.

1,000 feet long. Those gases which are not condensed pass, by flue 200 feet long, into a chimney 60 to 120 feet high. At Gawton the total length of flue between the furnace and chimney is about a English mile.

In working any description of furnace, it is important to observe that neither ore dust nor carbonaceous matters is allowed to go into the arsenious oxide; the latter would, when the arsenious oxide is sublimed, reduce some of it to metal. It is therefore necessary to

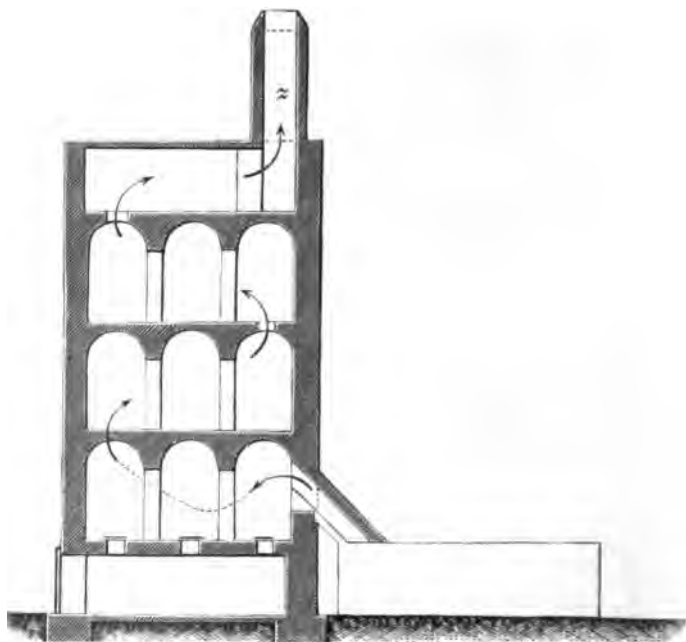


FIG. 455.

shut off the condensing arrangement from the furnace when the latter is being charged or emptied, and also when the charge is being rabbled or stirred. At these times the furnace is temporarily put into communication with a secondary chimney. The temperature should be only high enough to volatilise the arsenic, and the charge should be cautiously rabbled from time to time. When the charge ceases to give out any flame, the roasting is complete, and the charge is removed by gradually withdrawing it at the bridge. The time required for a charge depends on the amount of arsenic, iron and sulphur contained in the ore. The arsenious oxide is removed periodically from the flues and chambers.

In the muffle furnaces at Reichenstein in Silesia, which have been described above, 8 to 10 cwts. of arsenical pyrites, in the form of slimes, are roasted in a charge about 4 inches deep; the time required is 12 hours, and the coal consumed is 7 per cent. of the weight of the raw ore. The residue contains from 3 to 5 per cent. of arsenic, and is treated by Plattner's chlorine process for the recovery of the gold which it contains. The white arsenic collected in the condensers is either sold as such, or converted into arsenic-glass.

At St. Andreasberg in the Harz, native arsenic containing 65 per cent. arsenic, 4·5 per cent. lead, and 0·5 per cent. silver, was formerly worked in the cast-iron muffles already mentioned. The charges of 4 to 6 cwts. required 22 hours and the fuel (beechwood) consumed was 22 cubic feet. The arsenic obtained was all converted into vitreous arsenic. The residue amounted to 50 to 52 per cent. of the weight of the ore, and contained 1 to 2 per cent. of silver, and 12 to 16 per cent. of arsenic; it was treated to extract its silver.

At Ribas in Spain<sup>1</sup> charges of 20 cwt. used to be worked in muffle furnaces. They required 24 hours and consumed 4 cwts. of coal. In a reverberatory furnace with gas-fuel 3 tons of ore were roasted in 24 hours with 4 cwts. of coke.

At Freiburg<sup>2</sup> arsenious oxide is produced from ores containing lead and comparatively little arsenic (12 per cent. or less); dust containing arsenic from the flues of the other roasting furnaces is also used. Gas-fired furnaces are used as previously described, and coke is used as fuel, so as to get a flame free from soot. Each furnace is connected with a flue 820 feet long, for condensation. The charges vary according to the proportion of arsenic present, from 12 to 22 cwts., and the roasting lasts 5 to 8 hours. The residues, containing 1·5 to 2 per cent. of lead, are used for the extraction of that metal. The arsenious oxide of a grey colour, deposited in the nearer portions of the condensing flue, is purified by re-sublimation: the other portions are either sold as white arsenic or converted into arsenic glass.

In Cornwall and Devon 8 to 10 tons of ore are roasted in 24 hours, the coal used being 3 cwts. per ton of roasted ore. The furnaces have been described on page 610. Six men are required for each double furnace, working 8-hour shifts.

In the Brunton calciner described on page 610, 4 to 5 tons of ore are roasted in 24 hours; the tables make 5 to 10 revolutions in the hour, and the coal used is 1½ to 2 cwts. per ton of raw ore; 2 men

<sup>1</sup> *Berg- und Hütten. Ztg.*, 1853, p. 767.

<sup>2</sup> *Pr. Zeitschr.*, vol. xviii., p. 189.

working 12 hours each are sufficient to work the furnace during 24 hours.

In the Oxland furnace described on page 611, 20 to 25 tons of ore are roasted in 24 hours: the ores contain 15 per cent. of arsenic and require 1 cwt. of coal per ton of ore roasted: 3 men and 3 boys working 8 hours each are sufficient for the working of these furnaces per 24 hours.

At Bovisa<sup>1</sup> in the province of Milan, Italy, arsenical pyrites from the Cani mine near Monte Rosa, containing 34 per cent. of sulphur, 10 to 12 per cent. of arsenic, and 0.6 to 0.7 ounces of gold and 2.5 ounces of silver per ton, are treated for sulphuric acid, arsenious oxide and gold. They are roasted to this end, without addition of fuel, in a Malétra furnace, which is connected through a system of lead pipes and flues to a lead chamber, where the sulphur dioxide evolved in the roasting is converted into sulphuric acid. The arsenious oxide collects in the lead flues leading to the chamber and is removed at intervals. It forms a reddish-white mud and contains sulphuric acid and ferric oxide. Experiments have proved that pure arsenious oxide can only be obtained by resubliming this mud, after the sulphuric acid has been removed from it. To do this, the mud is brought on to a quartz filter and washed thoroughly with water. The filter stands on the false bottom of a rectangular brick-work box, and is covered with a perforated lead lid in order to distribute the washing water more evenly. The filtrates are run into the lead chamber; the mud is dried and then sublimed in a muffle furnace, yielding thereby a sublimate containing 98 to 99 per cent. of arsenious oxide ( $\text{As}_2\text{O}_3$ ). The pyritic residues contain 1.5 to 2 per cent. of sulphur and about 0.5 per cent. of arsenic. They are roasted dead in a shelf furnace with grate firing, and then treated for gold by the chlorination method.

### B. *The Refining of the Crude Arsenious Oxide*

In most cases it is necessary to purify the arsenious acid from foreign matter by resublimation: none but the purest ores yield at once marketable white arsenic. The commoner impurities are:—grains of ore, volatile constituents of the ores, flue dust and carbonaceous matter. Reverberatory furnaces with either gas or solid fuel are used, the former being preferable, as the arsenic produced in them is free from soot, ash-dust or cinders. Condensation

<sup>1</sup> *The Min. Ind.*, 1897, p. 40.

chambers or flues are attached to the furnaces to collect the arsenious acid.

At Freiberg, where comparatively impure flue-dust is worked, the gas-fired furnace previously described is used for the production of white arsenic. Charges of 12 cwt. are heated for 8 hours and yield 85 per cent. of their arsenic; the residues are worked up for lead: 10 to 12 cwts. of coke are used every 24 hours.

In Cornwall and Devon, where the crude arsenic contains about 70 per cent. of the oxide, furnaces similar to those used for roasting the ore are used.

Each pair of furnaces, having one long side in common, form one double furnace, the length and breadth being each 16 feet: each furnace has three working doors in its long side and the greatest height of the roof over the bed is  $1\frac{1}{2}$  feet. The fuel used consists of a mixture of coke and anthracite in equal quantities, and the gases and vapours leaving the furnace pass along a flue 100 feet long into a series of 12 chambers arranged in a zig-zag manner, each chamber being 7 feet high, 14 feet long and 4 feet wide, the total length of passage being 167 feet. From the chambers the gases pass into the chimney.

The foreign matter which accompanies the vapour is deposited in the flue leading to the chambers, whilst, in the latter, the arsenic condenses in crystals; these are ground in a mill like a flour mill and packed in wooden barrels.

At Deloro<sup>1</sup> in Canada, the crude oxide containing 85 per cent. of  $\text{As}_2\text{O}_3$  and 2 to 4 per cent. of sulphur, is resublimed in single hearth reverberatories which work off 3 charges of 1,600 lbs. each in 24 hours. The vapours pass first through a hot flue into a hot chamber, where the solid particles carried over (silica, &c.) are deposited, but the oxide remains in a vapourous state. They are then led into a cooling chamber, in which a deposit of oxide containing 99.6 to 100 per cent. of  $\text{As}_2\text{O}_3$  is produced, the only impurity being silica from the brickwork of the chamber. The pure oxide is withdrawn every fortnight; it is finally ground and is then ready for sale.

### C. The Production of White Arsenic Glass

White arsenic glass or vitreous arsenic is prepared by collecting the vaporised arsenic at a temperature so high that the sublimate fuses together into a mass.

There are two methods of procedure, *Glasmachen* and *Gröbmachen*.

<sup>1</sup> *The Min. Ind.*, 1903, p. 48.

The former, *Glasmachen*, is used when it is desired to change pure arsenious oxide into the vitreous form, the latter, *Gröbemachen*, when it is desired to purify the arsenious oxide first.

The plant is the same in both cases, and consists of cast-iron retorts heated by an open fire and attached to cylindrical receivers of wrought or cast iron. The retorts must be made of cast iron as free as possible from graphite; otherwise the carbon will reduce the arsenious oxide to suboxide of arsenic, and this will give the sublimate a grey colour.

The sublimed oxide collects on the walls of the receiver; at the top of the receiver is a sheet-iron hood connected by a sheet-iron

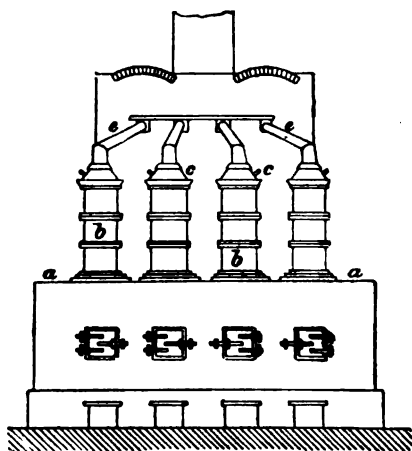


FIG. 456.

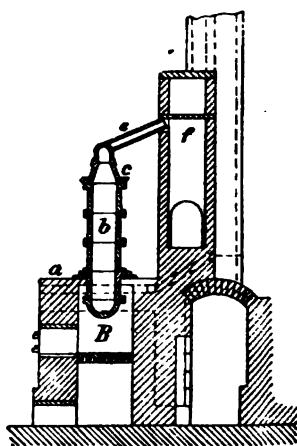


FIG. 457.

tube with a condensing chamber in which any uncondensed arsenious oxide collects.

Figs. 456 and 457 show the arrangement of the plant. *B* is the fireplace 3 feet wide, in which is suspended the retort *a*, 2 feet 5 inches deep, 2 feet in diameter and capable of holding a charge of  $2\frac{1}{2}$  cwt. of white arsenic. The wrought-iron receivers *b*, *b*, each in three sections, rest on the retorts, and are provided with handles. The joints are luted with a mixture of loam, hair and blood. At the upper end of the receiver is the leaden hood *c*, connected with the chamber *f* through the tube *c*.

When the *Gröbemachen* process is employed to purify the arsenious oxide before its conversion into the vitreous form, it is necessary to regulate the temperature so that there shall be no sintering of the

charge in the retort; otherwise the sintered oxide would not sublime over. When the correct temperature is employed the greater portion of the arsenic is obtained as a bulky, light sublimate on the walls of the receiver. The portions which escape through the receiver are condensed in the chamber beyond. The process is known to be ended when an iron bar, inserted through an opening in the hood, is no longer covered with a white deposit: the opening is closed by a tight-fitting door. When this point is reached, the fire is allowed to die out, and the sublimate removed to be converted into vitreous arsenic by the *Glasmachen* or "running" process.

The residue in the retort is returned to the ore-roasting furnaces. If it is desired to produce an impure arsenic-glass direct from an impure arsenious oxide, the temperature must be raised so high that the sublimate in the receiver fuses together. The product obtained in this way is known as crude arsenic-glass. It is of a grey colour, on account of the impurities in the arsenious oxide having passed over with it, and requires a further sublimation if white vitreous arsenic is to be made from it. The grey colour may be produced either by metallic arsenic, or by fine ore dust in the arsenious oxide employed.

For the *Glasmachen* or preparation of pure vitreous arsenic, the same apparatus is employed. The fire is urged to such a degree that the walls of the receiver are hot enough to fuse the sublimed arsenious oxide to a glass. If the temperature should be allowed to get too high, the amount of sublimed arsenic which passes into the chambers beyond the receiver is excessive; if it should not be high enough, the sublimate is powdery and loses its translucency. When the receiver is at the correct temperature, water hisses when sprinkled on the upper portion from a bunch of twigs, and instantly evaporates from the lower portion. The end of this process is tested in the way described above. The charges are  $2\frac{1}{2}$  to 3 cwt. each, and require 8 to 12 hours. At the end of the process the furnace is allowed to cool for 14 to 16 hours, and the vitreous arsenic is removed from the walls of the receivers, which it covers as a scale to a depth of from 1 to 2 inches.

The product is the amorphous modification of arsenious oxide, and when freshly prepared is transparent and glistening with a conchoidal fracture. After long exposure to the air it passes into the crystalline form and resembles porcelain, with a waxy lustre.

At St. Andreasberg in the Oberhartz,<sup>1</sup> crude arsenious oxide was

<sup>1</sup> Kerl, *Metallhüttenkunde*, p. 513.

formally worked in charges of  $2\frac{1}{2}$  cwt. into a crude arsenic-glass, and the latter converted in charges of  $3\frac{1}{2}$  cwt. into pure vitreous arsenic. Each sublimation took 8 to 12 hours, and yielded 89 per cent. of vitreous arsenic and 7 per cent. of residue, of which 40 to 60 per cent. was arsenious oxide. The 4 per cent. of apparent loss was partly actual loss and partly due to the powdery arsenic formed.

The consumption of wood fuel was 12 cubic feet per cwt. of glass produced.

At Ribas, in Spain, charges of 4 cwt. of purified white arsenic were worked in 7 hours; the fuel consumed was 150 lbs. wood and 74 lbs. coal per charge, and the glass obtained was 96 per cent.

At Freiberg the charges consist of  $2\frac{1}{2}$  to 3 cwts. each. The fuel consumed is 2 to 3 cubic feet per charge, and the time 8 to 12 hours: 87.5 per cent. of glass is obtained. The retorts used are about 23 inches in diameter and about 19 inches deep. The receivers are in three sections of about 23 inches diameter and a total height of about 38 inches. The top of the cover which closes the upper end of the receiver is  $5\frac{1}{2}$  inches in diameter, and is connected to a tube of the same diameter which leads into the condensing chamber. The life of a retort is about 150 charges.

### 3. THE PRODUCTION OF RED ARSENIC GLASS OR REALGAR

Realgar (also known as *ruby sulphur*, *arsenrubin*, *rauschroth sandarach*, &c.) is a combination of arsenic and sulphur which approaches in composition to native realgar. In colour it varies from rose to hyacinth red with an orange yellow streak. It is manufactured by subliming a mixture of mispickel and iron pyrites, or one of mispickel and sulphur. Both methods yield the same product, the two constituents being expelled by the heat and combining in the state of vapour.

If sulphur and arsenic be merely fused together, compounds are obtained which do not possess the desired colour; neither does the fusion of arsenic trioxide with sulphur yield realgar of the desired quality.

It is not essential, in order to obtain a good product, that the sulphur and arsenic should be employed in the correct molecular proportions. The best proportions for a product of any particular shade are discovered by trial.

The process consists of two distinct parts. The sublimation yields a product (*Rohglas*) of varying composition which is brought



up to the desired shade by further fusion with sulphur or arsenic. We shall therefore describe:—

A. The production of *Rohglas*.

B. The conversion of *Rohglas* into realgar or the “refining” of *Rohglas*.

#### A. The Production of “*Rohglas*”

The sublimation is carried out in a retort furnace. Usually the mispickel is mixed with an equal weight of iron pyrites. At Freiberg a mixture of the desired composition results from the preliminary mechanical dressing of the ores, whilst at other places it has to be specially prepared.

The furnace used at Freiberg contains 12 retorts in 3 rows; each retort is  $4\frac{1}{2}$  feet long, about 5 inches diameter, and 0·7 inch thick in the walls, and each is protected from contact with the flame by empty retorts placed under them. These latter are known as *Protecteurs*. Each furnace has two fireplaces. The charge is introduced at the rear of the retort, which is afterwards closed by a tile. The front end of the retort opens into a receiver fitted to it. This receiver is a sheet-iron box fitted with an opening for the escape of the steam liberated during the process; the progress of the operation can be watched through it.

At Freiberg the charge of iron and arsenical pyrites contains 10 to 15 per cent. of arsenic and 30 to 35 per cent. of sulphur, and a small quantity of silver, which is extracted from the residue after sublimation. A charge weighs about 60 lbs. and occupies only two-thirds of the retort.

The retort, when charged, is heated to redness for from 8 to 12 hours, after which the residue is drawn out. The residues still contain 0·5 per cent. of arsenic and 23 to 24 per cent. of sulphur, and are, after being roasted, added to a smelting charge for silver-lead. The receivers, which contain *Rohglas* in both the compact and pulverulent form, are emptied after each third charge. The massive *Rohglas* is treated by the refining process, while the pulverulent product is added to a subsequent charge to be again sublimed. Each furnace treats from 12 to 14 cwts. of ore in 24 hours with a consumption of 8 to 10 cwts. of coal; 6 furnaces are worked by each gang of 4 men working 8-hour shifts.

At Reichenstein<sup>1</sup> it was formerly the custom to work charges of 5 cwt. of arsenical pyrites and 87 lbs. of crude sulphur in glazed

<sup>1</sup> Fresenius, *Zeitschrift*, 1871, p. 308.

earthenware retorts, such as were used for the production of arsenic: each charge was worked off in 6 to 7 hours, and the yield was 168 lbs. of *Rohglas* per charge.

At Ribas<sup>1</sup> equal parts of mispickel and iron pyrites used to be sublimed in clay retorts. Each charge was 8 cwts. and yielded  $1\frac{1}{2}$  cwts. of *Rohglas*, the fuel used per charge was 2 cwt. wood and 3 cwt. coal, and the time required was 6 to 7 hours.

### B. The "Refining" of "*Rohglas*"

The first process is usually conducted so as to produce a *Rohglas* which shall be relatively rich in arsenic and poor in sulphur; and therefore, to bring it to the right shade, sulphur, as a rule, has to be added in the second process. It rarely happens that the opposite course is resorted to.

The refining is carried out in pans or pots of cast iron, provided with a discharge pipe at the bottom. The *Rohglas* is rapidly fused in these by quick firing, and then stirred. Impurities form a slag on the surface, known as refinery slag, and these are skimmed off and the requisite quantity of sulphur or arsenic, as the case may be, is stirred in with an iron bar.

As soon as the fused material runs freely from the iron bar and shows on cooling the requisite colour and compactness, the newly-formed slag is skimmed off and the refined realgar is run into conical, air-tight, covered moulds made of sheet iron. When cool, it is broken into pieces and at once ground to fine powder. The slag is used for the production of white arsenic.

At Freiberg, the pans used are  $16\frac{1}{2}$  inches in diameter and 23 inches deep, and the charge consists of 3 cwt. of *Rohglas* and 40 to 60 lbs. of sulphur. The process occupies 1 to 2 hours, and the product contains 75 per cent. arsenic and 25 per cent. of sulphur. Chilian mills are used for grinding.

At Reichenstein,<sup>2</sup> the charge used to be 4 cwt. of *Rohglas* with 30 per cent. of sulphur, which produced 479 lbs. of realgar.

At Ribas,<sup>3</sup> charges of 4 cwt. *Rohglas* were refined in iron pans in 2 hours each, by the addition of 45 to 56 lbs. of sulphur.

## 4. THE PRODUCTION OF ORPIMENT

This pigment, also known as *Rauschgelb* and *Auripigment* (corrupted into *orpiment*), consists of arsenious oxide coloured yellow by

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1853, p. 774.

<sup>2</sup> *Fresenius, loc. cit.*

<sup>3</sup> *Loc. cit.*

arsenic sulphide. It is really not the same in composition as the mineral known by the same name ( $\text{As}_2\text{S}_3$ ).

It is manufactured by subliming together arsenious oxide and sulphur, the proportion of the latter being determined by the shade required. The apparatus employed is that described above for the production of vitreous arsenic, the temperature of working being high enough to keep the sublimed orpiment liquid till the apparatus cools.

At Freiberg the process is as follows:—4·5 to 9 lbs. of sulphur are placed in the bottom of the retort, and 280 lbs. of white arsenic are placed on top of it; the mass is heated till an iron wire plunged in the melt is no longer coated when drawn out. During the process a portion of the arsenious oxide is reduced to arsenic by part of the sulphur present, sulphur dioxide being liberated. The reduced arsenic and the rest of the sulphur combine to form sulphide of arsenic, which is always contaminated with small quantities of free sulphur. The lowest receiver contains adhering to the walls, a fused mass of orpiment, varying in colour from citron yellow to orange red; the other receivers contain an irregular streaky product, which must be fused. A certain quantity of powdery product is also obtained which is added to subsequent charges for resublimation.

The charge of the above composition will yield seven-eighths of its total weight of orpiment in the solid or pulverulent form.

At Reichenstein, white arsenic with the addition of 5 per cent. of its weight of sulphur was formerly used for the preparation of orpiment.

Buchner<sup>1</sup> gives the following proportions of sulphur in different varieties of orpiment:—

	%S corresponding to % $\text{As}_2\text{S}_3$	
1. Very transparent, streaky . . . .	2·5	6·4
2. Twice refined, deep colour . . . .	1·05	2·68
3. Moderately strongly coloured . . . .	1·34	3·43

All these samples contained part of the sulphur uncombined, a small residue being left on treatment with ammonia.

When sulphuric acid which contains arsenic is purified by treatment with sulphuretted hydrogen, a sulphide of arsenic is obtained which corresponds in composition to the mineral orpiment: this method however is not well suited for the production of the pigment. When this precipitate was washed and heated in an iron retort in an atmosphere of coal gas the sublimate was an unsightly, dark-coloured glass which contained organic matter. At Freiberg it

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1871, p. 245.

is usual to work this product (from the purification of oil of vitriol by sulphuretted hydrogen) after drying it, by burning it in the kiln for the production of sulphur dioxide for sulphuric acid manufacture. the arsenic being obtained as arsenious acid.

## II. THE EXTRACTION OF ARSENICAL PRODUCTS FROM THE RESIDUES FROM THE MANUFACTURE OF COAL-TAR COLOURS

For this purpose a large number of methods have been proposed. The arsenic is principally in the form of arsenite or arseniate of lime, and the products aimed at are usually the two free acids. Most of the proposals depend on reducing the arsenic compound to the metallic state at a red heat by organic matter and burning the metallic vapour in air to form arsenious oxide.

*Winkler's Method.*<sup>1</sup>—The mother liquors from the magenta crystals are treated with soda in excess, in order to form arseniate of soda. The liquid is then evaporated in pans till crystals appear on its surface, after which it is mixed in boxes with powdered limestone and coal dust, and well stirred to form a solid mass: for every 100 lbs. of sodium arseniate in the liquid, 30 lbs. of limestone and 25 lbs. of coal are added. In the next process the limestone and coal together decompose the sodium arseniate; it is said that coal alone would not effect it. The mixture is next heated in a muffle with a double bottom. On the upper bed the water is driven off, and the dry mixture, when put on the lower one and heated to a red heat, gives off arsenic vapour, while sodium carbonate and lime remain behind. The arsenic vapour passes into condensing chambers where, meeting a current of air, it burns to arsenious oxide and is deposited. The sodium carbonate is extracted from the residue by solution and used again for the preliminary saturation. the lime also can be used again.

*Rando & Co's and Tambourin & Lemaire's Methods.*—The aniline residues are washed, dried and heated to redness with coke, the reduced arsenic which is liberated in the state of vapour is burnt, and the arsenious oxide collected in chambers.

*Bolley's Method.*—The residues are heated with hydrochloric acid or with salt and sulphuric acid. Arsenious chloride is given off and collected in water, when the greater part of the arsenic is precipitated as arsenious acid.

<sup>1</sup> *Deutsche Industrie-Zeitung*, 1876, p. 333, and *Verh. d. Vereins zur Beförderung des Gewerbf.*, 1876, part 3, p. 211.

*Stopp's Method.*—The residues are digested with hydrochloric acid in order to dissolve all the arsenic, the solution is then saturated with soda, and the arsenic is precipitated by adding lime. The precipitate is treated with sulphuric and nitric acids which convert the lime into insoluble gypsum, while the arsenic as arsenic acid remains in solution.

The author is not in a position to state how far any of these methods are in actual practice.

# NICKEL

## PHYSICAL PROPERTIES

NICKEL possesses an almost silvery-white lustre with a steel-grey tinge, and great brilliancy.

The specific gravity of cast nickel is given as 8.35, and that of rolled nickel as between 8.6 and 8.9.

With great hardness and capacity for taking polish it combines great malleability; it can be easily hammered, rolled, or drawn into wire. Sheets 0.0008 inch thick and wire 0.0004 inch in diameter may be made from it.

The tensile strength of nickel surpasses that of iron. According to Deville, a wire made from nickel containing 0.3 per cent. silicon and 0.1 per cent. copper bears a strain of 200 lbs., whereas a similar wire of iron breaks under 133 lbs. Kollmann examined a specimen of nickel from the manufactory of Fleitmann in Iserlohn, containing  $\frac{1}{10}$  per cent. magnesium, and found that its absolute tensile strength and extensibility were equal to that of Bessemer steel of medium hardness. The breaking strain was 87,110 lbs. per square inch, with an elongation of 15 to 21 per cent., and an elastic limit of 55,170 lbs. per square inch.

Nickel is attracted by a magnet, and then becomes magnetic itself: it is said to lose this property at 350° C.

Nickel can not only be welded to itself at a white heat, but it can also be welded to iron and certain alloys. Fleitmann is the inventor of the method of manufacturing nickel-plated wares by an application of this property. He welds iron and steel to pure nickel or to a nickel-iron alloy, and also welds nickel to alloys of copper and nickel. The method adopted is either hammering or rolling. For such welding to be successful, the necessary condition is the complete exclusion of air from the surfaces to be welded, which Fleitmann attains by various methods.

The coefficient of expansion of nickel between 0° and 100° C. is 0.001286 according to Fizeau; its specific heat is 0.1108.

Nickel is difficultly fusible. According to older experiments it melts at about  $1600^{\circ}\text{C}$ .; according to the newer work of Schertel between  $1392^{\circ}\text{C}$ . and  $1420^{\circ}\text{C}$ . According to Knut Styffe<sup>1</sup> its melting point is about  $1450^{\circ}\text{C}$ . It is more readily fusible if it contains carbon.

Molten nickel has the property of absorbing carbon monoxide and giving it out again on cooling. The alloys of nickel with copper also possess this property in a degree which increases directly with the percentage of nickel, and the temperature of the fused metal. Further, if certain substances (carbon and various oxides) are present in molten nickel, carbon monoxide is generated by action between them at certain temperatures. The occluded gas makes the nickel porous, and unsuitable for hammering and rolling. In order to obtain nickel free from blowholes, it is necessary to observe special precautions, to be described in the proper place.

Commercial nickel is exceedingly impure, being contaminated by substances of which even traces affect its valuable properties. The most harmful impurities are arsenic, sulphur, oxide of nickel and chlorine.

0.1 per cent. of arsenic makes nickel brittle, and incapable of being rolled.

0.1 per cent. of sulphur renders nickel unsuitable for rolling. It appears, from the results of experiments at the Berndorf Nickel Works at Vienna, that the same proportion of sulphur in alloys like German silver is harmless.

Iron in German silver lessens its extensibility and destroys this property altogether when the proportion of iron in the nickel used amounts to 1 per cent.

Nickel alloys containing much iron are especially remarkable for tenacity and strength, as was discovered in 1890. Nickel has the power of increasing the strength and elastic limit of iron. These alloys are used for armour plates and artillery.

Copper gives to nickel a yellow or brownish-red hue, but exerts no injurious influence on its properties as long as its proportion is less than  $1\frac{1}{2}$  times that of the nickel.

Cobalt increases the whiteness of nickel, and, up to a proportion of 6 per cent., has no influence on its tensile strength. A greater proportion is said to make the nickel brittle.

Carbon is dissolved by molten nickel, and seems not to affect its good qualities, so long as oxides are not present at the same time. It makes nickel slightly more fusible, but also brittle under certain

<sup>1</sup> *Oesterr. Zeitschr.* 1894, p. 340.

conditions. According to Jungk<sup>1</sup> the separation of carbon in the form of graphite from molten nickel takes place readily if the nickel contains a large proportion of cobalt. Carbon may be separated from nickel by silicon in the same way as it is separated from iron. According to Gard, commercial nickel may contain the greater part of its carbon in the separated form of graphitic scales. A sample of nickel produced by him, with 2.1 per cent. carbon (of which 2.03 per cent. existed as graphite) proved to be strongly magnetic, soft, and tolerably ductile. By passing marsh-gas over nickel he increased the proportion of carbon to 12 per cent., and this carbon seemed to be in chemical combination. Boussingault obtained, at a high temperature in a cementation furnace, a specimen of nickel, which held the same proportion of carbon as very hard steel, but all the essential properties of the original metal were retained. It therefore appears that nickel, unlike iron, is not hardened by the increase of its carbon. Nevertheless alloys of iron which are rich in nickel can be made harder by increasing their proportion of carbon (nickel-steel). According to Fleitmann nickel absorbs cyanogen, which makes it brittle.

According to Ledebur nickel absorbs its own monoxide, and this injures its tenacity and malleability, as cuprous oxide does that of copper. He also states that the percentage of oxygen (existing as monoxide) in brittle non-ductile cast nickel is 0.304; while in ductile nickel it is 0.084, and in cast German silver 0.061.

Ledebur also states that when nickel monoxide and carbon are both present in the metal, carbon monoxide is produced on fusion, and renders the castings unsound.

Nickel takes up silicon as iron does, when it is reduced from the oxide by carbon at a very high temperature in the presence of silica. Gard found in such nickel about 9.5 per cent. carbon, and 6.19 per cent. silicon. Nickel containing silicon has the physical properties of grey cast-iron.

Phosphorus, in the proportion of less than 0.3 per cent., exerts no injurious influence on the qualities of the metal. Above this proportion it makes it harder, and decreases its malleability.

Chlorine may be present to the extent of 0.18 per cent. in nickel separated in the wet way, and makes the German silver, for which such metal is used, unfit for rolling.

<sup>1</sup> *Dingler*, vol. 222, p. 94; vol. 236, p. 480.



## CHEMICAL PROPERTIES

Nickel is pyrophoric when reduced from its oxide by hydrogen at a comparatively low temperature. When prepared in other ways it is unaltered in either dry or moist air at the ordinary temperature. The quantity of carbon dioxide present exerts no influence. Heated in the air, it first assumes rainbow colours like steel does, and becomes covered, at a red heat, with a greenish grey coating of nickel monoxide, which is changed by strong heating into dull-green nickelo-nickelic oxide (hammer scale). In oxygen it burns as iron does, forming the monoxide.

Nickel at a red heat decomposes steam very slowly, as the metal becomes covered with olive-green crystals of the monoxide.

It is only very little acted on by hydrochloric or sulphuric acids in the cold. Dilute nitric acid and aqua regia dissolve it readily; concentrated nitric acid makes it "passive" like iron. This is supposed to be due to the formation of a coat of nickelo-nickelic oxide. Fused alkalis attack nickel but slightly; it is therefore used in laboratories for crucibles.

CHEMICAL REACTIONS OF NICKEL COMPOUNDS WHICH ARE  
OF IMPORTANCE IN ITS METALLURGY

## OXIDES

There are two oxides of nickel, and each forms a corresponding hydrate.

*Nickelous Oxide, NiO,*

or nickel monoxide, has a green colour. It is formed when nickel is heated in oxygen, in air, or in steam, as well as when nickel sulphide or arsenide is roasted; also by heating nickelous hydrate or sulphate.

At a strong red heat this oxide is reduced to metal by carbon or by carbon monoxide, the metal not melting. When reduced by carbon, carbon dioxide is chiefly formed; it is the only product of reaction when carbon monoxide is the reducing agent. Thus Boudouard<sup>1</sup> found in the first case (the carbon being in the form of wood charcoal) that at 550° C. 98.3 per cent. of carbon dioxide and 1.7 per cent by volume of carbon monoxide were formed; and at 800° C. 98.9 per cent. of carbon dioxide and 1.1 per cent. of carbon

<sup>1</sup> Recherches sur les équilibres chimiques, *Ann. Chem. Phys.*, vol. 24, p. 77, 1901.

monoxide. At the temperature of  $230^{\circ}\text{C}$ ., the powdered oxide is reduced to metal by hydrogen; and as before said, the metal thus prepared is pyrophoric. In mixtures of nickelous and ferrous oxide, the nickel is the first to be reduced by coal or carbon monoxide.

With silica this oxide combines to form silicates.

Whereas when cuprous oxide and copper sulphide are heated together in proper proportion the whole of the metal is separated and sulphur dioxide evolved, the heating of nickelous oxide with nickel sulphide produces no reaction.

If this oxide is heated with iron sulphide or arsenide, we get ferrous oxide and nickel sulphide or arsenide. In presence of silica the iron oxide will form a silicate.

Nickelous oxide and copper sulphide do not react.

It dissolves in acids, forming nickelous salts.

#### *Nickelous Hydrate, $\text{Ni}(\text{OH})_2$ ,*

is precipitated from solutions of nickel salts, by hydrates of the alkalis and alkaline earths. It is a bright green powder, converted by heating into the monoxide; all the nickel salts are derived from the monoxide.

#### *Nickelic Oxide, $\text{Ni}_2\text{O}_3$ ,*

or nickel sesquioxide, is black. It is obtained by gently heating nickelous carbonate or nitrate. Like the monoxide, it can be reduced to metal; and again like it, it does not react with the sulphide. No salts corresponding to it are known.

It dissolves in sulphuric and nitric acids, forming nickelous salts, and setting free oxygen; in hydrochloric acid it forms nickelous chloride and sets chlorine free; it also dissolves in ammonia with the separation of nitrogen.

The *hydrate* of this oxide is obtained by treating nickelous hydrate suspended in water with chlorine.

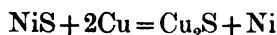
### NICKEL MONOSULPHIDE

is found native as *millerite* or *nickel pyrites* (*hair-pyrites*). It is obtained as a brittle bronze-yellow mass by heating nickel with sulphur; or as a powder, mixed with metallic nickel, by heating the sulphate strongly with coal, carbon monoxide or hydrogen.

The hydrated sulphide can be obtained as a brownish-black precipitate by the action of alkaline sulphides on nickel salts. The

is difficultly soluble in dilute hydrochloric acid. Small quantities dissolve in excess of the alkaline sulphide, imparting to it a brown colour. According to Mourlot<sup>1</sup> nickel sulphide is transformed into a sub-sulphide  $\text{Ni}_2\text{S}$  by an electric current of 35 ampères at 35 volts. Practically all the sulphur is driven off when it is subjected to 900 ampères at 50 volts.

Nickel sulphide is decomposed by copper, with the separation of metallic nickel, according to the following equations:—



When the sulphide is roasted, part of the sulphur passes off as dioxide, and the nickel is oxidised. A portion of the sulphur dioxide formed produces sulphuric acid, and forms nickel sulphate. Strong heating changes this last into nickelous oxide and sulphur trioxide (or sulphur dioxide and oxygen). By sufficiently long continued roasting at the proper temperature, nickelous oxide alone may be obtained; otherwise there will be a mixture of the oxide, the sulphate and unaltered sulphide.

If compounds, or mixtures, of nickel and iron sulphides are carefully roasted, a mixture of nickel monoxide and ferric oxide is obtained. As sulphate of nickel is a very stable compound, the roasting can be so conducted, if a sufficient quantity of sulphur be present, that the greater part of the nickel is obtained as sulphate, and the iron as ferric oxide. If the roasting is interrupted before all the sulphur is removed, a mixture of oxides, sulphates and sulphides of nickel and iron will remain.

By roasting nickel and copper sulphides in the same way, it is possible to get nickel monoxide and cupric oxide; or a mixture of oxides and sulphates as above mentioned. Again, as nickel sulphate is stable at a higher temperature than copper sulphate is, it is possible, with a sufficient proportion of sulphur in the ore, to conduct the roasting so that nickel remains chiefly as sulphate, and the copper as oxide.

If the three sulphides are used together, the same is true. Nickel may be obtained as sulphate, instead of as monoxide, while the other two metals appear as ferric and cupric oxides.

If a mixture of the oxides and sulphides of iron and nickel is heated with carbon and silica, nickel sulphide and ferrous silicate are

<sup>1</sup> *Compt. rendus*, 1897, 124, i. 768.

formed, if the proper proportion of sulphur is present; but if there is more sulphur present than can combine with the nickel, a mixture of ferrous and nickel sulphides is produced: this is known as nickel matte.

Similarly, if the mixture contains oxides and sulphides of the three metals, iron, copper and nickel, and if the correct proportion of sulphur be present, it is possible to regulate the fusion so that sulphides of nickel and copper, and ferrous silicate shall be obtained: if, however, there is too much sulphur present to produce that result, a nickel-copper matte is produced, which will contain the sulphides of all three metals.

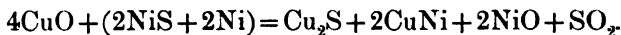
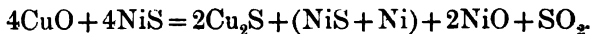
If a stream of air under pressure is passed through molten nickel matte containing silica, the iron combines with the latter, and sulphur dioxide is liberated, while the nickel sulphide is not affected.

If a current of air be passed through the remaining nickel sulphide, the nickel will be oxidised, and, in the presence of silica, will form a slag. Nickel cannot, therefore, be reduced from its sulphide by the use of a blast, in the same way as copper is separated by "Bessemerizing" copper matte.

The compound present in nickel-matte is always NiS. Nickelous sulphide,  $\text{Ni}_2\text{S}$ , does not exist therein; if the sulphur in a sample of nickel-matte is not sufficient for the formation of monosulphide, the excess of nickel will be in the metallic state. Molten nickel sulphide has the power of dissolving metallic nickel, which separates on cooling.

Nickel sulphide does not react with the oxides of iron.

According to Schweder<sup>1</sup> the sulphide and cupric oxide react as shown by the following equations:—



Nickel sulphide at a red heat is slowly and incompletely oxidised by steam.

Carbon and hydrogen decompose the heated sulphide very slowly, forming carbon bisulphide and sulphuretted hydrogen respectively. Carbon monoxide has no appreciable effect.

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 377; 1879, p. 17.

When the sulphide is melted with an acid iron silicate, a very small quantity of nickel passes into the slag.<sup>1</sup>

If cobalt sulphide is present a considerably greater quantity thereof passes into the slag.

If compounds or mixtures of iron, copper and nickel sulphides are melted with sodium sulphate and carbon, or with sodium sulphide, the iron and copper sulphides make, with the sodium sulphide, a matte in which there is only a small proportion of nickel sulphide; by far the greater portion of this last passes into a nickel matte with only a small quantity of the other two sulphides. The former matte is more easily fusible, and less dense than the nickel matte, and collects above it, so that the two kinds can be easily separated. Repeating the treatment in the same way on this nickel matte, iron and copper can be almost completely removed, and finally nickel sulphide obtained alone.

If any mixture of the three sulphides is roasted with common salt, the copper is converted into chloride, and the iron and nickel are oxidised. The chloride can be removed from the mixture of oxides by lixiviation, cupric chloride by water, cuprous chloride by alkaline chlorides, or weak hydrochloric acid.

#### NICKEL AND ARSENIC

Nickel has a great affinity for arsenic, and combines with it in very varying proportions. The compounds are known as nickel speiss.

If nickel arsenide is roasted, the arsenic forms arsenious oxide, the nickel sesquioxide. Part of the arsenious oxide escapes unaltered, part is further oxidised to arsenic oxide ( $\text{As}_2\text{O}_5$ ) and this combines with nickelous oxide to form an arseniate. Nickel arseniate is not decomposed when heated alone, so the result of the roasting is basic nickel arseniate.

This arseniate is reduced by carbon to a nickel arsenide which contains less arsenic than the one originally roasted. Such a reduction takes place, to a certain extent, during the oxidising roasting, by mixing the charge with powdered coal or carbonaceous substances (sawdust or pine-needles). By repeating the roasting a further proportion of arsenic is expelled, and by melting the product in a reducing flame a nickel arsenide containing less arsenic is again obtained. By a repetition of roasting and smelting under proper

<sup>1</sup> Badoureaux, *Ann. des Mines*, 1877, p. 237; *Berg- und Hüttenm. Ztg.*, 1878, pp. 185, 205, 228, 244-259.

conditions it is possible to reduce the arsenic in nickel to a very small proportion. The last portions may be removed by melting the compound with saltpetre and soda. The arsenic is thereby converted into sodium arseniate, which can be separated from the nickel monoxide by lixiviation.

Nickel speiss frequently contains iron, cobalt and copper. When this is roasted, a mixture of oxides, arseniates and undecomposed arsenides of these metals is obtained.

By stirring carbonaceous matter into the charge, iron arseniate is chiefly converted into ferric oxide, while the arsenic oxide is converted into arsenious oxide and arsenic suboxide, with the formation of carbon dioxide.

If sulphides are mixed or combined with these arsenides, sulphates are formed by roasting.

In addition to sulphates so formed, the arsenides themselves may be converted into sulphates by the vapours of sulphuric acid formed in the roasting.

Of the three metals, nickel, cobalt and iron, nickel has the greatest affinity for arsenic, then cobalt, lastly iron.

If a mixture of oxides, arsenides and arseniates of iron and nickel which contains sufficient arsenic to form  $\text{Ni}_2\text{As}$  with the nickel present, is heated with carbon and silica, the whole of the nickel will be converted into arsenide, and the iron into ferrous silicate. More than that proportion of arsenic will cause the formation of a nickel speiss containing iron arsenide.

Similarly if mixtures of oxides, arsenides and arseniates of nickel, cobalt and iron, which contain sufficient arsenic to form  $\text{Ni}_2\text{As}$  and  $\text{Co}_2\text{As}$ , are heated with carbon and silica, the nickel and cobalt will form arsenides and the iron will be slagged as ferrous silicate. If less than that amount of arsenic is present, some cobalt passes into the slag and carries with it a minute quantity of nickel, while more than that quantity of arsenic leads to the formation of cobalt-nickel speiss which contains iron arsenide.

Copper, in presence of carbon and silica, will, if sufficient arsenic be present, pass into the speiss more readily than iron; if the arsenic is not sufficient for this, the copper is either separated in the metallic state or passes into the slag as cuprous silicate.

If sulphur is present as well as copper in the mixture of oxides, arsenides and arseniates, the copper combines with the sulphur even when there is quite enough arsenic for its arsenide to be formed. If copper and sulphur are present in considerable proportions the sulphur compound forms a separate matte.

If nickelous and cobaltous oxides and cupric oxide are fused with silica and iron arsenide containing sufficient arsenic, a nickel-cobalt-copper speiss is produced, while the iron forms a ferrous silicate.

According to Badoureau,<sup>1</sup> when nickelous and cobaltous oxides are fused with arsenic or arsenical pyrites, almost the whole of the nickel and only part of the cobalt pass into the speiss.

If a nickel-iron speiss is fused, and air passed over it, the iron is oxidised first and converted into slag by the addition of silica. The nickel is oxidised only after the removal of the iron. The process can be so conducted that only the iron is removed, the nickel being left as arsenide. If cobalt is present in this speiss, it is oxidised and passes into slag after iron, but before nickel. The appearance of cobalt in the slag is detected by its blue colour. Therefore if it is desired to keep the cobalt in the speiss, the process of oxidation must be stopped as soon as the blue colour appears in the slag. As a certain quantity of nickel goes with the cobalt, the blue coloration shows also the presence of some nickel in the slag.

If heavy spar, instead of quartz, is added during this fusion, the iron may be completely separated, for heavy spar and iron arsenide react, forming iron arseniate and barium sulphide, both of which are taken into the slag. Any copper present is converted into sulphide by the barium sulphide, and separates as a matte if in considerable quantity.

### NICKEL SULPHATE

Nickel sulphate ( $\text{NiSO}_4 + 7\text{H}_2\text{O}$ ) is soluble in water. At a high temperature it is decomposed into nickel monoxide and sulphur trioxide, or, rather, sulphur dioxide and oxygen. It is more stable when heated than the sulphates of iron and copper. A mixture of all three sulphates can be heated so that the iron and copper compounds are broken up into the oxides, sulphur dioxide and oxygen, while nickel sulphate is almost all undecomposed, and can be separated from the mixed oxides by lixiviation with water, or, if it is the basic sulphate, with dilute acid.

If it is heated to redness with carbon, it is reduced to nickel sulphide, with the formation of carbon dioxide, but a portion of the sulphate is always reduced to metallic nickel, with the formation of carbon dioxide and sulphur dioxide; this nickel is retained in the sulphide.

<sup>1</sup> *Loc. cit.*

Carbon monoxide and hydrogen also reduce the sulphate to sulphide at a red heat.

From a solution of nickel sulphate, nickel is precipitated as sulphide by alkaline sulphides; as nickelous hydrate by potash, soda, milk of lime or milk of magnesia; and by sodium carbonate as basic carbonate.

It may be electrolysed, nickel appearing at the cathode, the acid radicle at the anode. The double sulphate with ammonium,  $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2$ , is used for nickel plating.

### CHLORIDE OF NICKEL

Nickel chloride is soluble in water. Its reactions are similar to those of the sulphate. The solution, when electrolysed, gives nickel at the cathode, chlorine at the anode.

### SILICATES OF NICKEL

Nickel silicates, when reduced by carbon, yield metallic nickel, if suitable bases are present to form a slag with the silicic acid. Nickel, like iron, dissolves carbon and silicon, and therefore, if a nickel silicate containing iron is smelted with carbon and fluxes, we have, by reduction of some of the iron, an iron-nickel alloy containing both carbon and silicon.

When the silicate is smelted with iron pyrites, with copper pyrites, or with sulphides of the alkalies and alkaline earths, nickel is reduced, and forms a matte or mixture of matte and metal.

If it is smelted with arsenic or arsenical pyrites, it is very incompletely converted into nickel speiss.

The mineral garnierite, a nickel-magnesium silicate, is soluble in sulphuric and hydrochloric acids.

### NICKEL CARBONYL, $\text{Ni}(\text{CO})_4$

This compound is formed if carbon monoxide is passed over nickel. It is prepared, according to Mittash,<sup>1</sup> when pure carbon monoxide acts upon nickel at the ordinary temperature, the reaction proceeding best at 30° C. It is a liquid of specific gravity 1.3 at 17° C., which freezes at -25° C., and boils at 43° C. (Mond), or 46° C. (Berthelot). Even at 36° C. it commences to decompose into nickel and carbon monoxide, the decomposition being complete at 180° C.

<sup>1</sup> *Ann. der Physik.*, 1902, vol. vii., No. i.



(Mond and Nasini). It is insoluble in water, easily soluble in alcohol, chloroform, hydrocarbons and ammoniacal copper solutions; it burns with a clear flame, and is very poisonous. Mond's process for the extraction of nickel depends upon the formation and decomposition of this carbonyl compound.

#### ALLOYS OF NICKEL

Nickel alloys with many metals, and it is principally used in the form of alloys, especially those with copper and zinc, known by various trade names, such as German silver, argentan, white metal, queen's metal, &c.; and the iron-nickel alloys ferro-nickel and nickel-steel. Silvered argentan is known as china-silver, packfong and Christoffe's metal. Other alloys of importance are those with aluminium, chromium and tungsten.

German silver usually contains 5 parts copper, 2 of nickel and 2 of zinc. Nickel alloys are employed for the subsidiary coinages of several countries; for instance, the coinages of Germany, the United States (since 1866), Belgium (since 1860), Brazil (since 1872), Venezuela (1877), are all 75 per cent. copper, with 25 per cent. nickel. In Chili the composition of the coins used since 1873 is 70 per cent. Cu, 20 per cent. Ni, 10 per cent. Zn.

At the present time a large quantity of nickel is used in producing "ferro-nickel," of which armour-plates, guns and other weapons are manufactured. It has been discovered recently that certain quantities of nickel added to iron materially increase its elasticity and tenacity.

Iron containing 0.3 to 0.5 per cent. of carbon and 3 per cent. of nickel has the highest elasticity; with 60 per cent. of nickel the highest tenacity, but when the nickel content is 30 per cent. the metal breaks under the hammer. The toughness diminishes with increase of nickel up to 16 per cent., when it is zero; it increases from that point up to 60 per cent. of nickel, when it is at a maximum, and then falls off with increasing percentage of nickel.

Addition of 2 to 5 per cent. of nickel to iron containing 0.3 to 0.5 per cent. of carbon increases the tenacity of the metal without lessening its toughness. This alloy is known as nickel-steel, and is used for the manufacture of armour plates (3 to 4.5 per cent. of nickel), turrets, gun shields, shafts and axles (2 to 2.5 per cent.), piston rods, crank shafts, boiler tubes, wire for electrical purposes, weapons &c. Ferro-nickel containing 25, 35, 50 and 75 per cent. of nickel, 1 per cent. of carbon, 0.3 of silica, 0.02 of sulphur, and 0.03 of phosphorus, is prepared in large quantity for use in

steel manufacture. Chrom-nickel containing about 73 per cent. of chromium, 23 of nickel, 2·5 of iron, 1 of carbon and 0·5 of silicon or sulphur, and tungsten-nickel of similar composition, are used also in steel manufacture.

In making ferro-nickel the nickel is added to the charge of iron in the Martin process, and may be used in the form of metallic nickel or monoxide. When small quantities of the oxide are used it is reduced by the carbon in the iron, but if large quantities are used, coal must be added for reduction.

It appears that the Carnegie Co. at Homestead<sup>1</sup> have bought a patent of their engineer's, according to which nickel monoxide, with more or less iron, is made into bricks with coal, or organic agglomerants, and charged into a Martin furnace.

By Harvey's method, used in the United States, plates of nickel-iron are converted by cementing into steel plates on one side only, after which they correspond in hardness and temper to iron and steel compound plates. The plates treated in this way resemble iron on one side, and steel on the other, and for this reason proved to possess valuable qualities.

The limited output of nickel (6,000 to 7,000 tons a year) stands in the way of its more extended application.

Nickel, when alloyed with metals more oxidisable than itself (e.g. copper), can be separated by an oxidising fusion.

## ORES OF NICKEL

Nickel occurs only in combination. In compounds it may be the chief element, or in small proportion to the other metals present.

In the extraction of the metal, not only nickel ores proper are important, but also those minerals which contain nickel in small proportion as a secondary element, or contain it, combined with other elements, as an impurity.

The greatest quantity of nickel is obtained at present from the silicate *garnierite*, or from magnetic pyrites containing nickel.

We may quote the following as true nickel ores:—

*Kupfernichel* or *arsenical nickel*,  $\text{NiAs}$ , containing 43·5 per cent. Ni. The nickel in this ore is often replaced by cobalt and iron in small proportion; the arsenic may be replaced by antimony up to 28 per cent., and in small proportion by sulphur. It has been found, or is still got, in Germany (Riechelsdorf, Olpe, Sangerhausen, Kamsdorf).

<sup>1</sup> V. Ehrenwerth, *Das Berg- und Hüttenwesen auf der Weltausstellung, Chicago*. Vienna, 1895.

Schneeberg, Annaberg Harzgerode, Wittichen); in Austria (Schladming, Leogang, Dobschau); in France (Allemont in Dauphiné, Balen in Basses-Pyrenées); in England (Pengelly, Fowey, St. Austell in Cornwall); and in Scotland (Bathgate).

*White nickel-ore*, or *chloanthite*,  $\text{NiAs}_2$ , is composed of 28.2 per cent. nickel and 71.8 per cent. arsenic. Frequently a small proportion of the nickel is replaced by cobalt and iron. This mineral is found in the same places as the other arsenide.

*Breithauptite*, or nickel antimonide ( $\text{NiSb}$ ), with 31.5 per cent. Ni (St. Andreasberg in the Harz); *ullmannite* or *nickel antimony glance* ( $\text{NiSb}_2 + \text{NiAs}_2$ ) with 26.1 per cent. Ni (at Siegen); *gersdorffite nickel glance*, or *nickel arsenic glance* ( $\text{NiAs}_2 + \text{NiS}_2$ ), with an average percentage of 35 Ni (Siegen, Schladming, Harzgerode, Helsingland); *annabergite*, *nickel ochre* or *nickel bloom* ( $\text{Ni}_3\text{As}_2\text{O}_8 + 8\text{H}_2\text{O}$ ) with 29.5 per cent. Ni (occurring in the upper seams of nickel-ore deposits); *moresonite* or *nickel vitriol* ( $\text{NiSO}_4 + 7\text{H}_2\text{O}$ ) (occurring similarly). All these ores occur in such small quantities that they can never be singly worked for nickel.

*Millerite*, or *hair pyrites*, *nickel pyrites*,  $\text{NiS}$ , with 64.5 per cent. Ni is occasionally found pure in large, independent masses, more often combined intimately with iron and copper pyrites. (At Nanzenbach near Dillenburg, Gap Mine in Pennsylvania, Sudbury in Canada, Arkansas.) This mixture of all three pyrites forms a valuable source of metallic nickel.

Iron and nickel pyrites, or *necopyrites* ( $2\text{FeS} + \text{NiS}$ ), with 18 to 21 per cent. Ni, is found at Lillehammer in Southern Norway.

*Garnierite* is a nickel magnesium silicate, containing water of crystallisation, discovered in 1863 by Garnier in the island of New Caledonia. It fills up clefts and fissures in a serpentine, formed by the metamorphosis of enstatite, a magnesium silicate, and is accompanied by several such silicates, by *chrysoprase*, and by *magnetite*, *chromite*, and other minerals. Its extensive occurrence in this locality has caused it to become the chief source of metallic nickel, after the nickel-holding pyrites (magnetic and copper) of Sudbury in Ontario. The usual composition of *garnierite* is—

9—17	per cent.	$\text{NiO}$ .
41—46	„	$\text{SiO}_2$ .
5—14	„	$\text{Fe}_2\text{O}_3$ .
1—7	„	$\text{Al}_2\text{O}_3$ .
6—9	„	$\text{MgO}$ .
8—16	„	$\text{H}_2\text{O}$ .

The average percentage of nickel in the ores may be taken as 10. The quantity of iron contained, which is only mechanically mingled, often exceeds the nickel. In the pure state, garnierite is either green or chocolate in colour; the green contains 45 to 48 per cent. of nickel monoxide, the brown variety 43 to 46 per cent. The darker the shade of green or brown the greater is the quantity of nickel in the mineral. The brown ore is even in greater quantities than the green ore. The mineral contains a small quantity of cobalt, though the quantity of this seldom exceeds 0.6 per cent.<sup>1</sup> The composition of garnierite varies according to the particular magnesium silicate which forms its basis. By the analyses of Garnier and Thiollier the composition  $(\text{NiMg})\text{SiO}_3 + n\text{H}_2\text{O}$  has been assigned to it. T. Moore gives the formula  $7\text{NiO}, 6\text{SiO}_2 + \text{H}_2\text{O}$ .

A nickel-magnesium silicate similar to this, containing 8.96 per cent. Ni in the impure condition, was discovered by Meissonier in 1876 in the province of Malaga in Spain. This occurrence is unimportant. Very recently, also, near Riddle Station in Oregon, a nickel-magnesium silicate has been found with an average of 5 per cent. of nickel.

Amongst nickel compounds of similar composition we have also *rewdanskite* at Rewdansk near Ekaterinenburg in Ural, *genthite*, occurring in Texas and Pennsylvania, and *pimelite* at Reichenstein in Silesia. These minerals are all found in such small quantities that they cannot form the foundation for a special extraction of nickel.

Nickel occurs with Serpentine in Silesia, north of Frankenstein (at Kosemütz, Züsendorf and Gläsendorf).

The composition is on the average:—

$\text{SiO}_2$	60—65 per cent.	$\text{Fe}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$	6—8.
$\text{MgO}$	8.5—12	Ni	2.3—3.5.

Loss on ignition, 8—15 per cent.

In places the ore is talcose in character and contains 4 to 18 per cent. of nickel. Nickel is extracted from these ores.

Among ores in which nickel is not the chief element we note especially certain pyrites, the chief being magnetic and copper pyrites. Many varieties of arsenical pyrites also contain nickel.

Iron and copper pyrites, as above, are found in the neighbourhood of Nanzenbach (before mentioned), Gladenbach, and St. Blasien and Totmoos in the Black Forest. The Nanzenbach ore has an average of 5 per cent. Ni and 5 per cent. Cu; St. Blasien ore 2 to 2.5 per

<sup>1</sup> *The Min. Ind.*, 1902, p. 488.

cent. Ni and 0.75 per cent. Cu. Magnetic pyrites containing nickel is found at Sohland in Lausitz, Saxony; in Sweden (Klefva and Smaland, Hudigswall, the neighbourhoods of Gefle, of Fahlun, and of Sagmyrna); in Norway (Langesund Fjord, Ringerick nickel-mine near Nakkerud, Kragerø, Moss, Snarum, Christiansand); in Piedmont (Varallo), Pennsylvania (Lancaster Gap Mine), Massachusetts (Dracut), Oregon, and largely developed in Sudbury (Canada). The proportion of nickel is, at Sohland 4 to 5 per cent. (along with 2 per cent. of copper), at Klefva 1.5 per cent., at Sagmyrna 0.5 to 0.8 per cent., Kragerø 1.75 per cent., Varallo 1.20 to 1.44 per cent., Gap Mine in Pennsylvania 1.75 per cent. (with 1 per cent. Cu and 0.1 per cent. Co). The copper pyrites at the Ringerick Mine in Norway contains 33.24 per cent. Cu, 0.42 to 1.75 per cent. Ni, and 0.01 per cent. Co. The magnetic pyrites (*pyrrhotite*) at Sudbury is found in large lenticular accretions in diorite dykes in the Laurentian and Huronian formations; it contains 1.5 to 9 per cent. Ni and is mixed with copper pyrites. The average amount of nickel is 3 per cent. and something over 3 per cent. is copper. As the depth of the deposit increases the percentage of nickel seems to increase, that of copper to decrease. For example in the upper levels of the Copper Cliff Mine the quantity of copper is 4 per cent., of nickel 4.5 per cent.; while at the deepest present level the quantity of copper has sunk to 0.5 per cent., and that of nickel has risen to 8 or 10 per cent.

The Sudbury ore is at the present time one of the principal sources of nickel.

The arsenical pyrites containing nickel at Dobschau in Hungary contains from 0.25 to 17 per cent. Ni; similar ore at Schladming in Styria contains 11 per cent. Ni and 1 per cent. Cu.

By far the largest amount of nickel is got at present from the garnierite ores of New Caledonia, and the magnetic pyrites of Sudbury in Canada.

## METALLURGICAL PRODUCTS USED AS A SOURCE OF THE METAL

When ores of lead, copper, cobalt or silver are smelted, any nickel which they contain collects in the speiss. Should the ore be free from arsenic, so that a speiss is not formed, the nickel will be found in the various intermediate products:—matte, blister-copper, tough pitch copper or lyes; or in final products like slags or bears; from all of these it can be extracted.

## THE EXTRACTION OF NICKEL

This may be done :—

- I. By the dry method.
- II. By the wet method.
- III. Electro-metallurgically.

The dry method should be used for ores and metallurgical products containing a large or a medium quantity of nickel, if it is possible to get a pure metal (or oxide) out of such ores, without the help of a wet method. It is also satisfactory when the purity of the product is not essential.

With poor ores the dry method can be used, if the nickel can be concentrated without great cost in an intermediate product (a matte or speiss), and if from this latter nickel or nickel oxide can be got pure without recourse to a wet method, or, again, if a pure metal is not the object.

Wet methods are used for ores which are poor in nickel, and for which concentration of the nickel in a matte or speiss would be economically impracticable.

Wet methods are also used for intermediate products, when it is desired to produce from sources of nickel in which copper is an impurity, a nickel oxide or metallic nickel which shall be free from copper; they are also employed when the desired products are more profitably obtained by these methods: such are the metal, alloys or salts.

Electrolytic methods are not applicable to ores, and have only recently been applied satisfactorily to alloys, with the object of preparing nickel free from copper, and salts of nickel from metallurgical products containing both copper and nickel.

Metallic nickel may contain many impurities, such as the oxide, and mechanically enclosed gases, which would restrict its application in the arts. In such cases a purification by some special refining process is necessary, and dry methods are generally used for this purpose. Most nickel smelters are in the habit of producing only a speiss or matte, which is further treated for the extraction and purification of the nickel by the manufacturers, who keep their processes secret.

Nickel monoxide has been manufactured in large quantities for the production of ferro-nickel: it is added, either alone or with a reducing agent, to charges of iron or steel. If it is used in small quantities with cast iron, there is usually sufficient carbon present in

the latter to act as a reducing agent. Nickel oxide is also used in the manufacture of pigments.

## I. EXTRACTION OF NICKEL IN THE DRY WAY

### A. EXTRACTION FROM ORES

The most important ores at present are the sulphur compounds and the silicates, the arsenic compounds taking the second place. Silicates are smelted with sulphuretted additions so as to produce mattes, which are treated like the mattes produced from sulphuretted ores.

#### 1. EXTRACTION OF NICKEL FROM SULPHUR COMPOUNDS

The compounds to be considered are magnetic and other pyrites containing nickel, frequently mixed with copper pyrites. They may be classified generally as compounds in which sulphur and iron are the chief elements, with, in addition, a small proportion of nickel and copper. The proportion of nickel varies between 1 per cent. and 5 per cent. Pure nickel sulphide, hair pyrites or millerite, does not occur in such quantities that it can be treated alone for nickel, but it occurs often in the above ores, and so finds its way into the smelting processes.

In smelting these ores in the dry way, after getting rid of gangue we are chiefly concerned with the separation of the nickel from sulphur and from iron, and in most cases also from copper. If no copper is present, the process becomes so much the simpler.

With ores free from copper and with mattes the extraction depends principally on the fact that iron has a greater affinity for oxygen than either nickel or sulphur has. Thus it is possible to remove iron from these ores as oxide, and slag it, the nickel being separated chiefly as sulphide. Then at a higher temperature atmospheric oxygen will convert this sulphide into monoxide, which must be reduced by carbon.

The formation of the sulphide is effected by roasting and smelting operations, the conversion to oxide by roasting, and reduction of the oxide by ignition with a reducing agent or smelting.

Owing to the small proportion of nickel in most ores (1 to 5 per

cent.) it is not possible to obtain the sulphide from them by a single smelting and roasting. It is most usual to adopt a procedure similar to that employed for the separation of copper from sulphide ores containing iron, and thus to produce, by roasting and subsequent reduction, a nickel-iron matte. This matte, containing iron but with an increased proportion of nickel, is converted by fusion in an oxidising atmosphere into a matte free from iron. But if this first matte is still poor in nickel, further concentration by the same methods takes place before the final treatment.

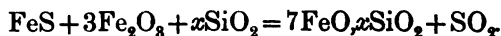
The matte obtained free from iron is subjected to dead roasting, often in two operations, and becomes nickelous oxide, which, as already said, is reduced to nickel by fusion with a reducing agent.

The first operation to which the ores are subjected, the roasting, converts all the metallic sulphides into a mixture of oxides, sulphates and undecomposed sulphides.

In the next process, the smelting of the roasted product in a shaft-furnace with carbon and siliceous matter, nearly all the iron passes into the slag, while any small proportion of iron sulphide still remaining undecomposed by both processes forms a matte containing all the nickel sulphide.

It is necessary to retain considerably more sulphur than is required to combine with nickel in the roasted product, because none of the small proportional amount of nickel present can be allowed to pass into the slag. Consequently the matte will contain a large quantity of iron sulphide. From this matte, known as raw nickel matte, the iron is separated, with the corresponding amount of sulphur, by an oxidising fusion in hearths, reverberatory furnaces or converters. If it is poor in nickel and rich in iron, it is better first to concentrate the nickel by another roasting followed by a reduction with carbon and silica as above, in a shaft furnace, or in a reverberatory furnace without reducing agent. The chemical changes with nickel coarse matte are just the same as with the ore direct, except that there is no longer any gangue to form slag.

When the roasted ore is smelted in a reverberatory furnace the ferric oxide present is reduced by the sulphur of the iron sulphide to ferrous oxide, in the presence of the silica, and sulphur dioxide passes off. The equation is as follows:—



Meanwhile the nickel monoxide present reacts with an equivalent quantity of ferrous sulphide to form nickel sulphide and ferrous



oxide, which latter forms slag. The product, then, of this smelting in a reverberatory furnace is nickel sulphide with a greater or less quantity of iron sulphide, according to the amount in the raw matte, and ferrous silicate.

If the matte or the concentrated matte, in the unroasted condition, is subjected to an oxidising fusion in a reverberatory furnace with silica, the iron will pass into the slag as ferrous oxide, while nickel sulphide is unchanged. Some nickel oxide reacts with ferrous sulphide and, as before, the results are nickel sulphide with more or less iron sulphide, and ferrous silicate.

In this process also an admixture of heavy spar and coal, or of Glauber salt and coal, works satisfactorily, as the coal causes barium or sodium sulphide to be formed, and this converts oxidised nickel back to sulphide, and the baryta or soda formed makes a very fusible slag with silica.

If the raw nickel matte or a concentrated matte is subjected to an oxidising fusion on a hearth under an air blast, the iron is oxidised to ferrous oxide and forms a slag with the silica of the furnace lining, while nickel sulphide is unchanged. If the oxidation is carried on sufficiently long, there will be only traces of iron sulphide left behind. But a considerable loss of nickel in the slag occurs if the iron is completely separated.

The separation of iron from nickel matte by means of the Bessemer converter is rapid and complete. Besides the iron, any arsenic and antimony present in the matte are completely removed. The iron is converted into ferrous oxide by the stream of air blown into the molten matte, and forms a slag with the silica of the converter lining, or else with quartz added. Any nickel which may be oxidised reacts with whatever ferrous sulphide may be left, thus giving ferrous oxide which is slagged, and nickel sulphide. The process finally gives this sulphide and a ferrous silicate which will always contain a certain quantity of nickel.

It is not possible to separate the nickel as metal in the converter by continuing the blast, as is done in separating copper from its sulphide in the copper-Bessemer process. In addition to the fact that nickel oxide and sulphide will not react, it is not possible at the temperature required in the process to oxidise the sulphur without oxidising the nickel as well. Indeed with a certain proportion of nickel and sulphur in the matte, nickel is more easily oxidised than sulphur. Finally, the heat developed in the oxidation of nickel sulphide is not enough to fuse nickel.

As nickel sulphide dissolves metallic nickel, a high concentration

of nickel can be attained by the converter process; the end product may in fact be a mixture of nickel and its sulphide. The matte enriched in this way and freed from iron is roasted dead and the oxide reduced with carbon.

The dead-roasting takes place in reverberatories, the reduction in crucibles, if the object be molten metal, or tubes and muffles, if spongy metal be desired. Thus the extraction of nickel from its copper-free ores embraces three processes, viz., treatment of ore for matte, removal of iron from the matte, and production of crude nickel from the nickel matte. If the nickel matte be poor in the metal, it is concentrated by roasting and smelting in shaft furnaces, part of the iron being eliminated in this manner.

When the nickel ore contains copper, as is generally the case, the copper remains in the matte owing to its great affinity for sulphur, and thus the oxidation followed by reduction gives a matte containing sulphides of nickel, iron and copper. If the matte is poor in nickel, it is enriched in that metal (and copper) by a roasting and smelting process, and the concentrated nickel-copper matte is deprived of the greater part of its iron by the converter process.

Several methods (secret so far as the details are concerned) are in use for the treatment of nickel-copper matte containing little or no iron. The Orford method consists in smelting the matte with Glauber salt and carbon; the copper then forms with the iron present a compound sulphide of sodium, copper and iron, and nickel sulphide remains behind. This is then roasted sweet and reduced.

The Mond process which is used at one English works consists in roasting the matte dead, extracting part of the copper with sulphuric acid, reducing the oxide of nickel to metal by means of reducing gases at a high temperature, and in passing carbon monoxide over the nickel at a certain temperature. The nickel carbonyl thus produced is decomposed at a higher temperature into nickel and carbon monoxide, and the latter used for preparing more of the carbonyl compound. Chloridising roasting of iron-free matte, lixiviation of the copper chloride and reduction of the residues have been suggested, but have never come into use.

Electrolytic methods have been used of late with advantage. The matte is roasted sweet, smelted for copper-nickel alloy and the latter electrolysed. This method may also be used for mattes containing iron.

The wet method of treatment consists in dead-roasting of the matte, extraction of nickel, copper and iron with acids, separate pre-

cipitation of these metals, and reduction of the oxide of nickel thus obtained with carbon.

If the object be to produce a copper-nickel alloy from matte free from iron, it is roasted sweet and the residue of nickel and copper oxides reduced by carbon.

The treatment of copper-bearing nickel ores for nickel in the dry way thus comprises the following operations :—

- a. Treatment of ore for nickel-copper matte.
- b. Removal of iron from this matte.
- c. Working up the iron-free matte for crude nickel.

If the first matte be very poor in nickel it is concentrated as described above, and if the object be to produce an alloy of copper and nickel, another process must be added to the above, viz. :—

- d. Treatment of iron-free nickel-copper matte for a nickel-copper alloy.

As the production of refined nickel mattes, both with and without copper, is carried out in the same way and with the same apparatus, it will be convenient to describe the production of nickel from sulphur compounds under the following heads :—

- a. Conversion of the ore into a coarse matte.
- b. Separation of iron from the latter, or “refining.”
- c. Working up of refined nickel matte into crude nickel.
- d. Working up of refined nickel-copper matte into crude nickel.
- e. Working up of nickel-copper matte into copper-nickel alloys.

#### a. THE CONVERSION OF THE ORE INTO COARSE MATTE

This process consists in roasting, followed by the reduction of the roasted product in shaft furnaces. In exceptional cases, when the ore is mixed with large quantities of earthy gangue, the roasting is dispensed with, and the unroasted ore smelted to get rid of the gangue as slag.

#### ROASTING THE ORE

The ore to be roasted is magnetic pyrites and iron pyrites, mixed with copper pyrites, and often with arsenic and antimony compounds, and also with silicates, quartz and earthy matter.

During roasting the aim is to get rid of sulphur until enough only remains to combine with nickel, copper and a portion of iron, during the smelting to follow. If cobalt is present it will be wholly combined with sulphur. Arsenic and antimony are removed as completely as possible.

We have seen already that as the proportion of nickel in the ore is so slight (1 to 4 per cent., rarely above 5 per cent.), it is inadvisable to decompose all the iron sulphide in roasting, for then in smelting nickel would pass into the slag with the iron; and further, as it is impossible in these circumstances to avoid the formation of iron sows, the nickel will be reduced and pass into them. It must depend on the relative proportions of nickel, cobalt, iron and sulphur in the ore, how much sulphur should be oxidised away. When possible, ores containing 4 to 5 per cent. nickel, or more, should be so worked that smelting gives a matte with 15 to 20 per cent. nickel without any serious loss of the metal. Poor ores with 1 or 2 per cent. should give a matte with 5 to 10 per cent.; for here loss of nickel in slag and sows has a greater proportional effect than with richer ores. If there is any cobalt in the ore, the roasting must be stopped so much the sooner. When the cobalt is worth separating there must be an excess of sulphur in the roasted product, for cobalt has less affinity for sulphur than nickel has, and so will pass into the slag before the latter does.

In the roasting the sulphur partly escapes as dioxide, and is partly converted into trioxide by contact with red-hot masses of ore and red-hot furnace walls. Iron, copper and nickel oxides combine with this trioxide to form the three sulphates. As the roasting proceeds and the temperature is raised, the sulphates are again decomposed into oxides and sulphur trioxide, or sulphur dioxide and oxygen. Iron sulphate is first decomposed, next the copper, lastly the nickel compound.

If the roasting were kept up long enough at the proper temperature, the product would be a mixture of ferric oxide, nickelous oxide and cupric oxide. But if it is stopped after a certain quantity of sulphur in the ore has been got rid of, as is nearly always necessary, in order to produce the matte, the product will be a mixture of oxides, sulphates and undecomposed sulphides. Ferric oxide, ferric sulphide and basic ferric salts preponderate in quantity. If zinc blende was present in the ore, zinc sulphide and oxide and neutral and basic sulphate are found in the product. If arsenic and antimony were present, arseniates and antimoniates are found as well as undecomposed arsenides and antimonides. We should find lead sulphide, oxide and sulphate resulting from galena in the ore. Quartz, heavy spar and silicates remain unaltered. Calcium carbonate will become sulphate.

*The Operation of Roasting.*—This may be carried on in heaps, kilns, shaft-furnaces, reverberatory furnaces, or muffles. The choice

among these methods depends on the necessity for disposing of noxious gaseous products, on the possibility of using these products in the manufacture of sulphuric acid, and on the cost of fuel and labour.

The roasting of lump ore in heaps takes a long time, is imperfect in its results for many ores, and provides no way of disposing of or utilising the gases set free; further, it causes loss of metal by the washing away of nickel and copper sulphates, unless it is carried on under cover; on the other hand, it means only slight cost of plant, a small amount of labour, and a small consumption of fuel, especially if the ore is rich in sulphur.

The fine ore ("smalls"), if it is not moulded into briquetts, serves as coverings and bottoms for the heaps of lump ore. The briquetting entails a good deal of labour, while roasting up to the required limit requires a definite proportion of lump to fine ore. Otherwise the roasting of fine ore in heaps has the same disadvantages as roasting lump ore.

This method is used when the utilisation of the gaseous products, for sulphuric acid or otherwise, is not feasible, on account of there being no market for the product, or because the nature of the ore is not suitable; and when, at the same time, the surrounding land is of so little value that it is unimportant whether it is injured by the noxious gases escaping; it may also be used where fuel and labour are dear. These conditions are met with in the chief place of roasting sulphuretted nickel ores, the neighbourhood of Sudbury in Ontario, and also to some extent in Sweden and Norway.

The Canadian ores are magnetic pyrites containing about 3 per cent. nickel and 3 to 4 per cent. copper. There is no sulphuric acid plant at Sudbury. The great compactness of the ore and its small proportion of sulphur are against its being roasted profitably in shaft furnaces, kilns, pyrites burners or Maletra furnaces, such as are used in sulphuric acid manufacture. To get gaseous products suitable for such manufacture, these ores must be mixed with others, or roasted in muffles. Further, it is not worth while to export an ore so poor in nickel to a place where its sulphur could be utilised. The best economy at present is to convert the ore into a nickel matte on the spot without concern for either utilising or rendering harmless the gaseous products. So the roasting of the ore is carried out simply in heaps. Only recently Sudbury ores have been sent to Saulte Ste. Marie to be roasted in Herreshof furnaces, heated with producer gas, along with pyrites from Michipicoten.<sup>1</sup> The sulphur

<sup>1</sup> *The Min. Ind.*, 1902, p. 492.

dioxide is used for the preparation of sulphite cellulose and part of it is liquefied. It was proved in 1902 that the roasting of ores with less than 25 per cent. of sulphur in the manner described was uneconomical. The sulphur dioxide in the furnace gases is so dilute, and the cost of heating the Herreshof furnace<sup>1</sup> is too great for the method to compete successfully with heap-roasting. We find similar conditions in Sweden at Klefva and Sagmyrna, and in Norway at the Ringerick nickel works, and at Kragerö, in which countries the nickel works are mostly at present out of work. The ore is poor, there is no market for sulphuric acid, and land is not dear. So here roasting in heaps is customary.

Roasting in stalls entails a great expenditure of time, like roasting in heaps; it means also a greater initial outlay and more labour and it endangers the health of the labourer during the emptying of the stalls. It precludes the utilisation of the oxidised gases, but steps are taken to diminish the noxiousness, by leading them into high chimneys. By careful management of the draught, the method will yield a more even roasting, and in a shorter time than roasting in heaps. The quantity of fuel used is as low for ores rich in sulphur as in heap-roasting; finely divided ore can only be used as bottoms and coverings unless it is briquetted.

Stall roasting is therefore used where the sulphurous gases cannot be utilised, but where their injurious effects are bound to be limited as far as possible by leading them into higher stacks.

Formerly these stalls were used at Dillenburg (the Isabella Works) and at the Sesia Works at Varallo, in Piedmont.

Shaft furnaces are used for ores rich in sulphur, both lump and fine, if the gases are to be used for sulphuric acid. This use of the gases presupposes such a proportion of sulphur and composition of ore that the roasting temperature can be kept up by the heat evolved by the oxidation of the sulphur, and that the ore is thoroughly burned through without leaving cores. The ore must not melt, nor even sinter, and the lumps of ore must not decrepitate at the temperature.

Shaft furnaces may also be used without any concern for the utilisation or rendering harmless of the furnace gases, if fuel is dear and labour cheap (the gases may be sent straight into the air or partly rendered less noxious by being led into high chimneys), or may be used when the ore must be rapidly roasted. In such cases lump ore may also be roasted in kilns; pulverulent ore in furnaces or

<sup>1</sup> *The Min. Ind.*, 1903, p. 490.

the Gerstenhöfer or Maletra pattern. In kilns, ores poor in sulphur are arranged in layers alternately with fuel.

The author is not aware of any instance of the use of shaft furnaces for the purpose of utilising the gases from nickel ores in sulphuric acid manufacture.

Shaft furnaces have been used at Dillenburg to roast ores of nickel. As the ore (pyrites containing nickel) was mixed with much gangue, the temperature had to be kept up by alternating with layers of fuel.

Roasting in reverberatory furnaces will not allow of the utilisation of the gases; it entails preliminary pulverisation of the ore, and a great consumption of fuel and labour, but it can be performed quickly and can be accurately adjusted to the right degree in getting rid of sulphur. Nevertheless, the costliness of this method has prevented its being used up till now for these sulphuretted ores containing so small a proportion of nickel. It becomes feasible with ores containing much nickel, and when a quick process is necessary, if utilisation of the gases is not desired, or is not suitable to the nature of the ore, in which cases as high a chimney as possible is used.

The use of muffles entails a large expenditure on fuel and labour, but it allows of the using, or rendering harmless, of the gaseous products and is convenient for stopping the roasting at the proper stage. With the muffles, as with the reverberatory furnaces, the ore must first be reduced to small size. Up till now they have not been used for these sulphuretted nickel ores because of the expense of the roasting. They may come into use when it is desired to utilise certain ores in sulphuric acid manufacture, which ores are not suitable for roasting in shaft furnaces, either because of their small proportion of sulphur, or because of their sintering, fusing or decrepitating.

### *Roasting in Heaps*

This is carried on in the same way as the normal roasting of magnetic pyrites, or of pyrites containing copper.<sup>1</sup>

At Sudbury, in Canada, the ores, magnetic pyrites with about 3 per cent. nickel and rather over 3 per cent. copper, are broken and classified into the three sizes, 4 inches,  $1\frac{1}{4}$  inch, and  $\frac{3}{4}$  inch, and then piled on a bed of wood in heaps of 5 to 15 feet high, 82 feet long, and about 39 feet broad. A heap contains from 600 tons to 3,000 or more. In the middle there is a small chimney to create a draught and carry off the products of combustion. To every

<sup>1</sup> Vol. i. p. 31.

20 tons of ore a cord of wood (128 cubic feet) is allowed. The bed is laid upon a layer of fine ore 6 to 10 inches thick, which itself becomes roasted down to a certain depth, generally about half-way. On the bed the coarsest pieces are laid, then the medium-sized, and lastly, fine ore again. The whole heap is covered with a layer of fine ore 6 to 8 inches thick. The length of time for the roasting varies according to the size of the heaps from 6 to 20 weeks. A heap containing 1,000 tons takes 60 to 80 days. By one roasting the proportion of sulphur in the ore is reduced from 30 or 40 per cent. to between 4 and 7 per cent.<sup>1</sup>

At the works at Klefva in Småland (Sweden), closed at present, the nickeliferous magnetic pyrites was subjected to a single roasting in heaps on a bed of wood, each heap containing 210 tons.<sup>2</sup> This pyrites contains from 1.08 to 2.03 per cent. nickel, and from 0.38 to 1.03 per cent. copper. At Sagmyrna (also closed) the pyrites, containing 0.6 per cent. nickel and 0.7 per cent. copper, was roasted three times. Each heap held 300 or 400 tons of ore, and burned 3 or 4 weeks.

At the Ringerick works in Norway (also closed) magnetic pyrites with from 0.42 to 1.75 per cent. nickel was roasted with wood in heaps of about the same size of those at Sagmyrna; they burned for from 1 to 3 months. After roasting, the ore was sorted, and that which was imperfectly roasted put into another heap with fresh ore.

### *Roasting in Stalls*

This form of roasting used to be carried on at the Isabella Works at Dillenburg, and the Sesia Works at Varallo in Piedmont. At the former place stalls have been replaced by shaft furnaces.

At the Sesia Works,<sup>3</sup> the pyrites contained from 1.20 to 1.44 per cent. of nickel. It was roasted in stalls about 13 feet long, 10 feet broad, and 10 feet high, with two fires. The charge in a stall was 60 to 80 tons. Two tons of wood were required to roast it.

### *Roasting in Shaft Furnaces*

At the Isabella Works, which have been closed for a long time, the pyrites (averaging 3 per cent. of nickel, 5 per cent. of copper) was roasted in kilns about 6 feet 6 inches high, 4 feet 6 inches square in

<sup>1</sup> *The Min. Ind.*, 1894, p. 459.

<sup>2</sup> 3,000 Swedish centners, each 94½ lbs.

<sup>3</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 185.



section at the upper end, and 2 feet 3 inches square at the lower end. The pyrites was laid in layers alternately with lignite to assist the combustion. The gaseous products were conducted into a chimney 40 feet high, and from 2 to 3 tons of ore were roasted in 24 hours.

At the Gap Mine in Pennsylvania (now worked out), the magnetic pyrites with 1.75 per cent. Ni, 0.1 per cent. Co, 1 per cent. Cu, was roasted in kilns.<sup>1</sup>

#### SMELTING OF THE ROASTED ORE TO PRODUCE COARSE NICKEL MATTE

Matte can be produced directly without roasting when ores poor in sulphur are used. This was formerly done at Kragerö in Norway, where the pyrites containing 1.25 per cent. of nickel was disseminated in a finely-divided state in the rock. Generally, the ores must first be roasted. They then contain a mixture of oxides, sulphates and undecomposed sulphides of nickel, copper and iron, and the greater part of the nickel and of the copper is combined with sulphur. As a rule, metallic arsenides and antimonides, arseniates and antimoniates, quartz, silicates and gypsum are found here. Frequently there are small quantities of cobalt as sulphide, oxide and sulphate.

In the smelting of this ore with carbon and fluxes, iron should be slagged as far as possible, and nickel, cobalt and copper collected into a matte. The iron passes into the slag through the reduction of ferric oxide to ferrous, and the combination of this with silica; and also by the decomposition of iron sulphide by nickel oxide, in the presence of silica and carbon. This is also brought about by copper oxide when present. Thus the nickel and copper oxides become sulphides and a corresponding amount of iron becomes silicate. Also nickel silicate, generally formed to a certain extent, undergoes a double decomposition with iron sulphide. Copper silicate will behave in the same way. Cobalt silicate is not decomposed by iron sulphide to form cobalt sulphide. Part of the oxides of nickel and copper becomes reduced to metal by carbon monoxide and carbon. Metallic nickel dissolves in the sulphide of nickel present; copper combines with sulphur taken from iron sulphide. Iron will then be separated as metal, unless the iron sulphide is reduced to the combination  $\text{Fe}_2\text{S}$ , a compound not yet isolated. Until the existence of this compound is proved it is better to assume that iron is reduced to metal. This will dissolve in the ordinary monosulphide as nickel does in its sulphide. Further, any ferric oxide present may be reduced

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1874, p. 142; 1875, p. 58.

by the metal to ferrous oxide, and so pass into slag. Another portion of copper oxide reacts with sulphide, as in the English copper smelting process. The copper thus set free will take sulphur from iron sulphide, just as above. Nickel sulphate will be reduced to sulphide, unless the heat decomposes it into nickel monoxide, sulphur dioxide and oxygen. The same applies to copper sulphate. Part of the iron sulphate is decomposed into ferric oxide, sulphur dioxide and oxygen; carbon monoxide converts the rest of it into ferrous oxide and sulphur dioxide, carbon dioxide being formed.

All these sulphides of nickel, copper, iron, and occasionally cobalt, whether newly-formed by the decomposition of sulphates, or originally present in the roasted ore, unite to form a matte. So long as a considerable amount of iron sulphide is present, there can be but a small quantity of nickel as silicate in the slag, for the double decomposition mentioned above takes place almost completely. The same will apply to copper, but any cobalt silicate produced will remain in the slag.

Antimonates and arseniates are reduced to metal, and partly volatilise as such. In the presence of undecomposed pyrites part of the arsenic is volatilised as sulphide. The remaining arsenic and antimony, if they are only in small quantities, pass into the matte; otherwise they form a speiss, combined chiefly with nickel and cobalt. Any gypsum will be reduced to sulphide of calcium, which acts with nickel and copper oxides like iron sulphide does.

The quartz and silicates pass into slag. In case the oxide of iron in the charge is not enough to slag it completely, basic slags from a subsequent process or basic ores are added, while if the base preponderates in the charge quartz and argillaceous ores are added, or acid slags. If the ores have been roasted too strongly, so that it is to be feared there will be nickel in the slag, they are mixed with unroasted ore; and ores which have been insufficiently roasted, and which would in consequence yield a large quantity of matte poor in nickel, are mixed with slags which contain nickel.

Whenever possible the mixing is arranged so as to give a matte with 15 to 25 per cent. nickel. But with the usual ores, poor in nickel, a matte with a lower percentage must be aimed at.

The slag may contain neither too much nor too little silica.

Excess makes the slag less fusible, and in its pasty condition small portions of matte are mechanically enclosed in it; also it requires a great expenditure of fuel, and the raised temperature causes the reduction of iron in the charge. In the same way as iron is reduced in the blast furnace from oxides and even from silicates,

so in this charge, which is difficultly fusible owing to its great proportion of silica, iron will be separated as metal, and with it a portion of nickel. This metal sticks fast to the walls of the shaft furnace as "sows," and the accumulation of these constricts and ultimately "freezes up" the furnace. In practice the slag is never allowed to contain much above 42 per cent. of silica.

Too little silica, which is the same as too much iron, in the slag makes its density greater, so that it is difficult to separate it from the matte, portions of which are mechanically enclosed. If the furnace is of masonry the brickwork is acted upon, and the slag, from its basic nature, is able to take up the silica and acid silicates. But further, iron is readily reduced from this slag so rich in iron, and again sows are formed in the furnace, and shorten the duration of a campaign. Although too small a proportion of silica is not so injurious as too much, in practice it is advisable not to let it sink below 24 per cent., the lowest limit being 18 per cent.

As determined by practice, the most judicious percentage of silica is between 24 and 36 per cent.

As to the class of silicates present in the slag, they are between mono- and bi-silicates, the chief base being ferrous oxides. In some cases there may be only mono-silicate, or a mixture of sub- and mono-silicates. Lime, magnesia and alumina may be present as bases to a certain extent, besides ferrous oxide. A relatively small quantity of magnesia and alumina will make the slag refractory, while lime may be present in larger quantity.

The smelting of the ore takes place in shaft furnaces. Very recently these have been constructed like the new shaft furnaces for smelting roasted ferriferous copper ores,<sup>1</sup> with circular, elliptical or rectangular horizontal section. By their use the same advantages are obtained as when they are used for copper ores, namely greater output and a greater economy of fuel. Furnaces of this sort are therefore used largely for smelting roasted nickel ores containing sulphur. At the Canadian Copper Co.'s works in Sudbury a Herreshof furnace is used with a water-jacket, 8 feet 10 inches high, 6 feet 3 inches in the longer side, and 3 feet 3 inches in the shorter side of a section of the furnace at the level of the tuyeres. In this furnace 125 tons of ore are smelted in 24 hours. At the works of the Ludwig Mond Co. at Victoria, near Sudbury, 200 tons of ore are worked off in 24 hours in a water-jacketed furnace, 19 feet high from the floor level to the charging level, and 3 feet by 10 feet in area at the tuyere level.<sup>2</sup>

<sup>1</sup> Vol. i. p. 129.

<sup>2</sup> *The Min. Ind.*, 1902, p. 494.

The height of the furnace depends on the amount of iron in the charge, and the kind of fuel. The higher the furnace, the easier will reduction of iron take place. The greater the amount of iron therefore the lower the furnace. When wood charcoal is used the furnaces are built higher than with coke under similar circumstances, because the combustion of wood charcoal draws strongly upwards, and thus with a low furnace part would be burned uselessly at the top.

Usually the height varies from  $6\frac{1}{2}$  to 20 feet. With coke it seldom goes beyond  $14\frac{1}{2}$  feet, from bottom to throat; with wood charcoal it may be 20 feet. The height from the tuyeres up to the throat is from  $6\frac{1}{2}$  to 10 feet with coke, from 13 to  $16\frac{1}{2}$  feet with wood charcoal. In the Herreshof furnace at Sudbury, with water-jacket and elliptical cross section, and burning coke, the height from the tuyere level to the throat is  $6\frac{1}{2}$  to 10 feet; the height of the water-jacketed furnace at Victoria is 13 feet.

The cross section should be circular, rectangular or oval. The pressure of the draught varies between  $\frac{1}{2}$  inch and 2 inches of mercury, except in extraordinary cases. The diameter of the furnace, or the shorter side of the rectangle, at the level of the tuyeres, is from 2 feet 6 inches to 4 feet 4 inches, and a little greater at the throat. It varies according as the ore is more or less fusible, and as the pressure must be low or high. (For the structure and dimensions of the furnace see under copper smelting.<sup>1</sup>)

The tuyeres are distributed as symmetrically as possible round the circumference of the tuyere level. In old furnaces the tuyeres were in the back wall of the furnace. The blast is supplied usually by a Root's blower, and is only exceptionally (as at Victoria, Sudbury) heated for fear of promoting reduction of the iron.

The arrangement of the furnace, when there is much iron present, is best as *Spurofen*, for if the molten mass remains too long in the furnace, there will be a separation of iron, and sows may form on the furnace walls. The receivers (*Spurtiegel*) to collect the matte are lined with brick, or brasque of clay and coal-dust. Iron cannot be used, as it is readily acted on by the matte.

In Sweden (Klefva, Sagmyrna) furnaces have also been used built on the *Sumpfofen* pattern.

The construction of the water-jacket furnace used at Sudbury is shown in Figs. 458, 459.

*X* is the water-jacket made of steel plate. The water space, *x*.

<sup>1</sup> Vol. i. p. 129.

within it is about 2 inches wide. *U* is the blast-pipe. The furnace is built with an independent forehearth (*Spurofen*). The molten mass flows out of the furnace through the water-jacketed pipe *i*, made of bronze, into the receiver *T* carried on wheels. The receiver is surrounded by a water-jacket at the sides, has a movable lid and a fire-clay bottom. The slag runs out at the upper exit *S* (slag-notch) while the matte is tapped through the tap-hole *t*, provided also with a water-jacketed

bronze pipe. The bottom of the furnace is formed of a circular plate, on top of which is a thin layer of sand, and then a course of fire-brick. Above this a portion of the fused charge, reaching to the lower level of the tap-hole, is allowed to solidify, and over this latter the fused mass flows through the tap-hole into the receiver.

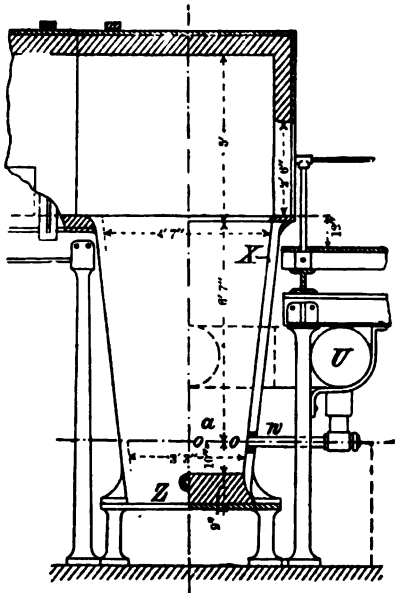


FIG. 458.

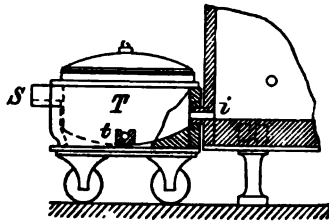


FIG. 459.

During the working the molten mass is continuously above the tap-hole, so that the blast cannot blow out there. During the tapping the slag hole is stopped by clay, so here also the blast cannot escape. In other furnaces of this kind the horizontal section has the shape of a rectangle with rounded corners. At the tuyere level the long side is 6 feet, the short side 3 feet. The tuyeres are twelve altogether, five in each long side, one in each short side. The height of this furnace from tuyeres to mouth is about  $6\frac{1}{2}$  feet. The furnaces

the Mond Co. in Sudbury<sup>1</sup> are rectangular in section and are surrounded by water-jackets 8 feet high made of steel plate. The side plate is  $\frac{1}{2}$  inch thick, the outside one  $\frac{1}{4}$  inch thick, and the space between is 6 inches wide. Above the jacket there are vertical brick walls 5 feet high and 9 inches thick. The sectional area of

<sup>1</sup> *The Mineral Industry*, 1902, p. 494.

the furnace is 10 feet by 3 feet at the tuyere level, and 10 feet by 5 feet 8 inches at the upper end of the water-jacket; the height from the bed to the charging level is 18 feet, and the tuyere level is 5 feet 8 inches above the furnace bed. There are 8 tuyeres on each long side and the arrangement is that of a *Spirofen*. The furnace bed is formed of a cast-iron plate covered with fire-proof material, and rests on 12 cast-iron pillars 3 feet high. The distance between the bed-plate and the water-jacket is 22 inches. Both slag and matte are collected in a movable receiver made of steel and lined with fire-proof material, the dimensions being: diameter 9 feet, height 3 feet 6 inches. There they separate according to density, the slag running off at a certain level through a copper spout, the matte being tapped from time to time. The furnace gases pass through a flue dust chamber; the blast produced by a blower is warmed by traversing a chamber above this and separated from it by steel plates.

The working is carried on just the same as in the smelting of roasted copper ores. The products are matte and slag. If the charge contains much iron, iron sows will form containing a considerable quantity of nickel. The matte contains from 15 to 25 per cent. of nickel. Formerly the mattes produced from poorer ores containing 0·4 to 2 per cent. of nickel had only 3·25 to 10 per cent. of the metal, and such mattes had to be concentrated. These poor mattes are produced in Sweden, Norway and Piedmont; the smallest proportion, 3·25 per cent., being found in the matte formerly produced at Kragerö, in Norway,<sup>1</sup> where the ores (with 1·25 per cent. nickel), consisting of finely divided magnetic pyrites, were smelted without roasting.

At Klefva in Sweden,<sup>2</sup> the ores had the following composition:—

	First quality. Percentage.	Second quality. Percentage.
Ni . . . . .	2·03	1·08
Co . . . . .	0·10	0·07
Fe . . . . .	57·68	43·24
Mn . . . . .	0·12	0·20
Cu . . . . .	0·38	1·03
S . . . . .	33·52	24·45
SiO <sub>2</sub> . . . . .	0·40	14·75
Al <sub>2</sub> O <sub>3</sub> . . . . .	0·20	4·32
CaO . . . . .	0·12	2·73
MgO . . . . .	0·09	2·04

The matte produced contained:—

	Percentage.
Ni . . . . .	4·70
Cu . . . . .	2·30
S . . . . .	31·05
Fe . . . . .	61·95

<sup>1</sup> Balling, *Metallhüttenkunde*, p. 570, and above, p. 520.

<sup>2</sup> *Ibid.*, p. 568.

The matte obtained at Sagmyrna from similar ores contained 5 per cent. nickel.

The magnetic pyrites used at the Ringeriges Works,<sup>1</sup> Norway, contained from 0.42 to 1.75 per cent. nickel, and the matte formed from it from 5 to 6 per cent. nickel, and from 3.6 to 3.8 per cent copper. According to Schweder<sup>2</sup> the composition of the matte was :—

	I.	II.
S. . . . .	26.5	28.30
Fe . . . . .	59.62	55.30
Ni . . . . .	5.7	6.01
Cu . . . . .	3.65	3.80
Residue . . . . .	3.88	5.92

At the Sesia Works, Piedmont, the pyrites contained 2.2 per cent. nickel, the matte 7 per cent.; such poor mattes are seldom produced at the present day.

At the Isabella Works at Dillenburg the ore formerly used, which consisted of iron pyrites containing nickel, copper pyrites and serpentine, contained 3 per cent. nickel and 5 per cent. copper; the matte had the following composition :—<sup>3</sup>

	Ni.	Cu.	Fe.	S.
I. . . . .	19.44	22.30	35.20	22.00
II. . . . .	14.30	14.92	44.90	28.04
III. . . . .	18.11	13.39	42.46	26.04
IV. . . . .	13.03	16.55	42.80	27.82

At Sudbury, at the present time, the matte contains 15 to 25 per cent. nickel.

The specimens of this matte sent to the Chicago Exhibition contained—<sup>4</sup>

Ni . . . . .	18—25 per cent.
Cu . . . . .	20—25 "
Fe . . . . .	25—35 "
S . . . . .	20—30 "

Ahn gives the composition of a Sudbury matte as <sup>5</sup>

Ni . . . . .	15.5 per cent.
Cu . . . . .	27 "
Fe . . . . .	30 "
S . . . . .	26 "
Co, Pt, Ag, Au . . . . .	1.5 "

<sup>1</sup> Schweder, *Berg- und Hüttenm. Ztg.*, 1879, pp. 18, 79, 106, 122.

<sup>2</sup> *Ibid.*, *Berg- und Hüttenm. Ztg.*, 1878, p. 423.

<sup>3</sup> Schnabel, *Preuss. Zeitschr.*, 1866, p. 108.

<sup>4</sup> V. Ehrenwerth, *Das Berg- und Hüttenwesen auf der Weltausstellung in Chicago*, Wien, 1895.

<sup>5</sup> V. Ehrenwerth, *loc. cit.*

The average composition of the matte produced in Sudbury at the works of the Canadian Copper Company in the year 1902 was:—<sup>1</sup>

Cu	=	13·2 per cent.	Ag	=	1·90 ounces per ton.
Ni	=	17·8 „	Pt	=	0·35 „ „
Co	=	0·45 „	Pd	=	0·35 „ „
Fe	=	42·00 „			
S	=	21·4 „			

Sulphur in nickel matte forms protosulphides with copper and silver ( $\text{Cu}_2\text{S}$ ,  $\text{Ag}_2\text{S}$ ), and monosulphides with nickel and iron ( $\text{NiS}$ ,  $\text{FeS}$ ). If, as is often the case, there is not enough sulphur to form these two latter sulphides, the excess of the metals is dissolved in their monosulphides when in the molten condition, according to Schweder's researches.<sup>2</sup> On cooling they separate out. According to Schweder the existence of any sub-sulphides of nickel and iron is improbable.

The composition of the slags lies between mono- and bi-silicates, as already mentioned; and it may even decrease in proportion of silica to a mixture of sub- and mono-silicate. With good management the slags should contain so little nickel that they can be thrown away. The author can offer only a very few complete analyses of slag.

A slag formerly produced at the Isabella Works had the following composition:—<sup>3</sup>

$\text{SiO}_2$	38·56 per cent.
$\text{Al}_2\text{O}_3$	7·61 „
$\text{FeO}$	35·64 „
$\text{CaO}$	13·55 „
$\text{MgO}$	4·79 „

The proportion of nickel is not given: it is said to have been very small and only mechanically enclosed in the form of matte.

The slag at the Ringeriges Works in Norway contained 0·108 per cent. Ni, and 0·08 per cent. Cu according to Schweder.<sup>4</sup>

The slag at Sudbury is said to possess a composition between mono- and sesqui-silicate, and to contain between 27 and 38 per cent. of silicon and 43 to 46 per cent. of ferrous oxide; the copper and nickel each range from 0·3 to 0·4 per cent. One specimen contained:—

$\text{SiO}_2$	38 per cent.
$\text{FeO}$	43 „
$\text{CaO}$	4·5 „
$\text{Al}_2\text{O}_3$	10 „
S	2 „
Ni	0·45 „
Cu	0·4 „
$\text{MgO}$	2·5 „

<sup>1</sup> *The Min. Ind.*, 1902, p. 493.

<sup>2</sup> Schweder, *Berg- und Hüttenm. Ztg.*, 1878, p. 409.

<sup>3</sup> Kerl, *Metallhüttenkunde*, p. 542.

<sup>4</sup> *Loc. cit.*



These slags are partly thrown away, partly added again in similar smeltings, or in the concentration processes for the matte.

The iron sows are chiefly composed of metallic iron, mixed with nickel and copper, and also with sulphur, carbon, silicon, arsenic and antimony compounds. Iron and nickel are produced by the reduction of their oxides, or by separation from the fused matte which often contains excess of these metals.

An iron sow from Dillenburg contained:—

Ni . . . . .	4·85 per cent.
Cu . . . . .	1·40 „
Fe . . . . .	88·17 „
Co . . . . .	0·05 „
S . . . . .	4·05 „
SiO <sub>2</sub> . . . . .	2·11 „

One from the Ringeriges Works contained, according to Schweder:—

S . . . . .	10·34 per cent.
Ni . . . . .	18·11 „
Cu . . . . .	2·7 „
Fe . . . . .	68·85 „

If nickel is to be extracted from these sows, they are exposed to a blast on hearths, or smelted in reverberatory furnaces with metallic sulphides, or worked up by wet methods.

#### EXAMPLES OF THE SMELTING OF ROASTED ORE INTO MATTE.

Mention may be here made first of the smelting of ores in small furnaces, as performed formerly at Dillenburg, and in Sweden, Norway and Piedmont. This is now only of historical interest. After this the treatment of Canadian ores in large furnaces, as employed at present at Sudbury in Canada, will be described.

At the Isabella Works<sup>1</sup> the ores were roasted in kilns; they contained before roasting 3 per cent. Ni and 5 per cent. Cu, the gangue being calcspar and diorite. They are smelted for matte in a low blast furnace, 5 feet high, 2 feet 4 inches broad, and 2 feet 4 inches deep, which was constructed as a *Spurofen* with double slag notches (the so-called *Brillenofen*). It had one tuyere in the back wall, and was worked with a “nose.” The blast pressure was from 0·6 to 0·65 in. of mercury. The charge consisted of 100 parts roasted ore and 63 of ore slag. In 24 hours 2·2 tons of roasted ore were smelted. The consumption of coke was 70 per cent. of the matte produced. Out of 100 parts of ore, 30 of matte were obtained with from 13 to 19 per cent. Ni. The composition of the slag is given above.

<sup>1</sup> Schnabel, *loc. cit.*

At Klefva in Sweden,<sup>1</sup> the ores above mentioned with from 1·08 to 2·3 per cent. Ni, after a previous roasting in heaps, were smelted in *Sumpff* furnaces with five tuyeres, coke and wood charcoal being the fuel. The furnaces had an oblong horizontal section about 4 feet broad by 3 feet 3 inches deep. The forehearth extended 3 feet beyond the breast of the furnace. The height of the coke furnace was 12 feet 6 inches, that of the wood charcoal furnace 19 feet 6 inches. The charge was roasted ore with some unroasted ore, impure ore-slag, and slag from the concentration of matte. In 24 hours 34 tons of charge were treated. Out of this, 6·3 tons of matte were obtained, containing 4·7 per cent. nickel. There are no figures given for fuel consumption. The length of a campaign was 2 months when coke was used, 6 months with wood charcoal. According to Badoureau, the ores at Sagmyrna in Sweden<sup>2</sup> contained in the unroasted state 0·6 per cent. of nickel and 0·7 per cent. of copper; they were roasted in heaps and then smelted in furnaces, trapezoidal in horizontal section, 13 feet 6 inches in height (12 feet 6 inches from the level of the tuyeres to the mouth), and 3 feet 2 inches across from front to back. The number of tuyeres was 5, three in the back wall, and one in each side wall. (The other measurements, the blast-pressure and the type of furnace are not stated in the original paper). In 24 hours 10 to 12 tons of ore were smelted, but the consumption of fuel is not stated. The resulting matte contained on the average 4 per cent. of nickel and 4·5 per cent. of copper.

At the Ringeriges Works,<sup>3</sup> the raw ore contained on the average 1·73 per cent. of nickel, 0·81 per cent. of copper, and 30 per cent. of gangue. It was roasted in heaps, and smelted in shaft furnaces 6 feet 6 inches high, 3 feet 3 inches deep, 3 feet 3 inches wide, constructed as *Sumpffofen*, with 3 tuyeres (1 in the back, 1 in each side); the matte contained from 5 to 6 per cent. of nickel, and from 3·6 to 3·8 per cent. of copper. The charge contained:—100 parts roasted ore, 25 parts slag, 21 parts coke.

The quantity put through and the blast pressure are not given. A campaign lasted three weeks. After this time the bed of the furnace was so thickly encrusted with sows of iron that the work had to be suspended until they were removed.

At Kragerö, in Norway,<sup>4</sup> ores which unroasted contained 1·25 per cent. Ni were smelted in blast furnaces about 8 feet high, refinery slag being added to them (slag from the refining of the

<sup>1</sup> Balling, *Metallhüttenkunde*, p. 566.

<sup>2</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 186.

<sup>3</sup> Schweder, *loc. cit.*

<sup>4</sup> Dingler, vol. 229, p. 376.

matte), and the resulting product contained  $3\frac{1}{2}$  per cent. of nickel.

At the Sesia Works (Varallo in Piedmont)<sup>1</sup> the ores were siliceous, and contained from 1.2 to 1.44 per cent. of nickel. They were smelted in *Brillenöfen*, 6 feet 6 inches high, 20 inches wide, and 24 inches deep, with one tuyere in the back, 2 inches diameter at the nose, with a blast pressure of  $1\frac{1}{2}$  in. mercury. The matte contained 7 per cent. of nickel. In 1878 the charge consisted of:—100 parts roasted ores, 28 parts limestone, 25 parts clay, 37 parts slag from the concentration or refining process; 15 parts coke were used to 100 parts charge. In 24 hours 5.4 tons of charge were put through. 100 parts ore gave 32 matte, and 150 slag.

At Sudbury<sup>2</sup> the ores contain on the average 3 per cent. of nickel, and undergo a single roasting in heaps. They are then smelted in Herreshof water-jacket furnaces, round or elliptical, constructed as *Spuröfen*, and provided with a movable fore-hearth running on wheels. These furnaces are from 6 feet 6 inches to 10 feet high from the tuyeres to the mouth. To the ores is added a slag containing nickel from the Bessemerising of the matte. The product contains from 15 to 25 per cent. of nickel, and from 20 to 27 per cent. of copper. The water-jacket keeps the temperature so low that the formation of iron sows is much diminished or altogether avoided.

At the works of the Canadian Copper Company<sup>3</sup> 125 tons of ore are smelted in 24 hours in Herreshof furnaces about 9 feet high, 6 feet 3 inches in the longer side, and 3 feet 3 inches in the shorter side, at the level of the tuyeres. The consumption of fuel is 15 per cent. The roasted ore has such a composition that no additions are necessary. The 15 tons of matte obtained contain from 13 to 27 per cent. of copper, from 15 to 23 per cent. of nickel, and from 20 to 30 per cent. of sulphur. From selected rich ores a matte is frequently obtained with 52 per cent. of nickel. At present there are nine furnaces at work and 900 tons of ore are smelted daily.<sup>4</sup>

At the works of the Ludwig Mond Company, Victoria, Sudbury,<sup>5</sup> 125 tons of ore were put through in 24 hours at a blast pressure of 3 ounces. The furnaces were rectangular and water-jacketed, 18 feet 4 inches in total height, 12 feet 6 inches from the tuyeres to the throat, 3 feet by 10 feet in the clear at the tuyeres, and 3 feet

<sup>1</sup> Badoureaux, *Annales des Mines*, 1877, p. 237. *Berg- und Hüttenm. Ztg.*, 1878, p. 186.

<sup>2</sup> Knut Styffe, *Oester. Zeit.*, 1894, p. 309. Ehrenwerth, *loc. cit.*, p. 368.

<sup>3</sup> *Mineral Industry*, p. 459, 1894. *Trans. A.I.M.E.*, 1889. Levat, "Mémoires sur les Progrès de la Métallurgie du Nickel," *Ann. des Mines*, 1892.

<sup>4</sup> *The Min. Ind.*, 1902, p. 492.

<sup>5</sup> *Ibid.*, p. 494.

by 5 feet 8 inches at the upper end of the mantles. Reduction of blast pressure increases the working capacity, and it is thought possible to raise the quantity put through to 200 to 250 tons a day. The charge consisted of 1500 to 1800 lbs. of ore, 400 to 750 lbs. of quartzose ore poor in nickel, and 0 to 600 lbs. of converter slag. Each charge weighed about 2500 lbs. and required 300 lbs. of coke, the consumption of the latter being 12 per cent. of the ore.

#### **b. THE REMOVAL OF IRON FROM THE COARSE MATTE, OR ITS REFINING**

The removal of iron from nickel and nickel-copper matte with consequent enriching in nickel and copper can be brought about by roasting the mattes and smelting the product in shaft furnaces or reverberatories, or by an oxidising smelting of the matte in hearths, reverberatories or converters. It is not possible to remove all the iron thereby: a certain quantity, generally under 1 per cent., remains, so that the enriched matte is not strictly iron-free.

Concentration before refining is necessary in the case of such mattes containing but little nickel, as are frequently produced. This concentration consists in an oxidising roasting, followed by smelting in shaft furnaces or (less often) in reverberatory furnaces; it may be brought about in one operation by an oxidising smelting in a reverberatory furnace.

Although concentration is seldom resorted to now, since the mattes from the ore-smelting are generally of such a nature that they can be refined straightway, yet the description of the concentration process can hardly be left out; so that we have to consider:—

- (a) The preliminary treatment of the matte on concentration.
- (b) The refining of the matte.

#### **a. CONCENTRATION OF POOR MATTE**

This consists in an oxidising roasting, followed by a smelting of the product with coal, and bodies containing silica, in blast-furnaces, or in reverberatory furnaces; or else in a single operation only—an oxidising fusion in a reverberatory furnace. The roasting must be conducted so that in the subsequent reduction the greater part of the iron passes into the slag, leaving the whole of the nickel and copper and part of the iron in the matte. The nickel and copper content of this should be enriched as far as is possible without slagging any considerable amount of nickel. Only most exceptionally is the concentration process repeated on this product.

*Roasting the Coarse Matte*

This roasting can be conducted in heaps, stalls, shaft furnaces, reverberatory furnaces or muffle furnaces.

The chemical changes are the same as on roasting the ore. The product consists of a mixture of nickel monoxide, cupric oxide, ferric oxide and magnetic iron oxide, undecomposed sulphides and small quantities of sulphates.

*Roasting in heaps* has the disadvantages already detailed under roasting of ore. The gaseous products are discharged into the air, and as repeated operations are required, much valuable capital is thus compelled to lie idle. It has the advantage that the roasted product passes into the blast furnace in large pieces. It is best if carried on in sheds protected by a roof, to avoid the washing away of nickel and copper sulphates by rain. The operation is conducted similarly to ore roasting; but as the amount of sulphur is smaller, and the quantity of material available is less, the heaps are also smaller than ore-heaps (from 50 to 200 tons). For a complete desulphurisation of the matte three or five burnings are usually required. In the last one combustible material (wood and wood charcoal) is laid in layers in the heaps, to obtain sufficient heat. The well roasted part of the ore is picked out after each burning, the superficial layers and the badly roasted parts, after the pieces are broken up, are made up with badly roasted ore from other heaps to form a new heap. The bed of the heap is made of brushwood, and coal, or of billets of wood. The heaps burn several weeks or months, according to their size and the amount of sulphur in the matte.

Such roasting in heaps can take place only in places where the noxious gases may be passed into the air, and where sulphuric acid has no value. Such was the case in Sweden and Norway.

*Roasting in stalls* is not cheaper than in heaps, and endangers the health of the workers when the stalls have to be emptied. Nevertheless with a right management of the air-supply it can be carried on more quickly than the other method, and it possesses this advantage, that all noxious effects of the gases can be lessened or removed by the use of high chimneys. By this method, too, the roasted matte enters the furnace in large pieces. Here again several burnings are necessary if the sulphur is to be completely got rid of.

These stalls have been used in Sweden, Norway and Piedmont. In Klefva<sup>1</sup> each held 50 tons matte. The roasting lasted 5 or 6 weeks. In Sagmyrna (Sweden) a stall held 25 tons, and the matte went through four or five burnings.

<sup>1</sup> Balling, *loc. cit.*

In the Sesia works at Varallo<sup>1</sup> the matte was roasted four times in stalls, in charges of 20 tons. Each roasting lasted 5 to 8 days. At the last roasting coke was introduced in layers. One ton of wood was used to roast 20 tons of matte.

At the Scopello works in Piedmont<sup>2</sup> there were Wellner stalls for the roasting of matte. These are stalls without a grate, but with a sloping bottom, which has fireplaces in one of the narrower sides. The length of a kiln was from 8 to 10 feet inside, width 10 to 11½ feet.<sup>3</sup> It had four fireplaces, and held about 25 tons of matte. The matte at these works required two to four burnings. The roasting of one charge lasted 15 hours.

*Roasting in shaft furnaces* is suitable when the gases have to be rendered innocuous, or can be converted into sulphuric acid. The necessary condition is that the matte should not sinter easily. In that case the roasting of this matte can be carried on in kilns in a similar way to the roasting of copper and lead matte. Up till now this method of roasting has not been used.

*Roasting in reverberatory furnaces* is the best way if the gaseous products can be ignored. The roasting is completed in the shortest time, and it can be stopped at the exact point desired. Nevertheless, it has the drawbacks that there is a comparatively large consumption of fuel, and that the matte must be in small pieces, and therefore passes in this form into the blast furnaces for smelting. The noxious effect of the gases is diminished by the use of very high chimneys.

The same sort of reverberatory furnaces that are described in Vol. I. for the roasting of copper matte are suitable for this roasting. Such a method was used at the Isabella works at Dillenburg.<sup>4</sup>

The matte there contained from 13 to 20 per cent. Ni, from 16 to 23 per cent. Cu, and from 22 to 27 per cent. S. It was roasted in hand-worked short reverberatory furnaces of the form and dimension of the lower portion of the old double Mansfield furnace. A charge of half a ton was roasted in 10 hours; for this half ton one-fifth of a ton of coal was needed, and 71 per cent. of the sulphur was got rid of in the roasting.

The roasting is carried on with greater advantage in long-bedded calcining furnaces, and mechanical calciners, than in those of the ordinary type.

*Muffle furnaces* facilitate the use of the gases for sulphuric acid manufacture; but, like reverberatory furnaces, they entail a preliminary reduction of the matte to small size, and a large consumption of fuel.

<sup>1</sup> Badoureaux, *Berg- und Hüttenm. Ztg.*, 1878, p. 186.

<sup>2</sup> Badoureaux, *loc. cit.*

<sup>3</sup> See vol. i. p. 43.

<sup>4</sup> Schnabel, *loc. cit.*

Up till now they have not been used for this purpose. They would be suitable if the gaseous products were to be utilised, and for a matte that sinters easily and so does not lend itself to roasting in a shaft furnace.

### *Smelting of Roasted Coarse Matte into Concentrated Matte*

This smelting is carried on in blast furnaces or reverberatory furnaces. It consists in the smelting of oxides, sulphates and undecomposed sulphides of the various metals. Reverberatory furnaces are used in England; the others in Scandinavia and on the Continent. Reverberatory furnaces have this advantage, that iron sows are not formed in them.

### *Smelting of Roasted Matte in Blast Furnaces*

The furnaces are of the same type as for ore smelting. They must not be too high, as otherwise the reducing action of the carbon monoxide is too powerful, so that sows are formed. To decrease the probability of sows the furnace is arranged as a *Spurofen*, generally a double gutter furnace with two eyes, the so-called *Brillenofen* or "spectacle" furnace. The fixed fore-hearth and the crucible arrangement are both conducive to the formation of sows.

For the slagging of the iron, acid slag from the working of the ore is added, or quartzose ore, or ore mixed with acid silicates in such a way that a monosilicate slag results. The blast pressure is 0.6 to 1.2 in. mercury. The chemical changes are just the same as in the smelting of roasted ore, except that there is no earthy matter to pass into slag.

The products are concentrated matte, slag, and frequently iron sows as well. If this concentrated matte is still poor in nickel, as used to be the case at some of the Scandinavian works, the processes of roasting and smelting must be repeated. In this repetition the iron, down to a small fraction, is separated from the matte, and this latter is dead roasted and afterwards converted into copper-nickel.

At Dillenburg, at the Isabella works, the coarse matte contained from 13 to 19 per cent. Ni, from 14 to 22 per cent. Cu, and from 35 to 44 per cent. Fe. The concentrated matte obtained from it had the following composition:—<sup>1</sup>

	I.		II.		III.
Cu . . . . .	34.49	. .	35.68	. .	49.66
Ni . . . . .	28.69	. .	32.93	. .	30.19
Fe . . . . .	15.58	. .	13.03	. .	9.24
S. . . . .	21.15		18.17		10.91

<sup>1</sup> Schnabel, *loc. cit.*

At present mattes containing 13 to 19 per cent. of nickel and 14 to 22 per cent. of copper are treated directly for refined matte.

At Klefva, in Sweden, the concentrated matte contained from 52 to 57 per cent. Ni; 22 to 28 per cent. Cu.

At Sagmyrna, in Sweden, its composition was: from 25 to 26 per cent. Ni, from 25 to 30 per cent. Cu, 26 per cent. Fe, and from 25 to 30 per cent. S.

At Kragerö, in Norway: 30 per cent. Ni, and 15 per cent. Cu.

At Sesia works, Piedmont: from 28 to 32 per cent. Ni, from 48 to 52 per cent. Fe, and 20 per cent. S.

At St. Blasien: from 24 to 26 per cent. Ni.

In such concentrated matte, nickel and iron exist partly as monosulphides, partly as separated metals dissolved in these. In the cooling of the fused matte the metals frequently separate out in large crystals. A very poor concentrated matte was produced at the Ringeriges works, in Norway.<sup>1</sup> The original coarse matte contained 5 or 6 per cent. nickel; the concentrated, only from 10 to 12 nickel and from 7 to 10 per cent. copper; apparently this resulted from very incomplete roasting of the matte. According to Ebermayer the slag from the concentration process from the Aurora works at Gladenbach had the following composition:—<sup>2</sup>

Silica . . . . .	39.368
Alumina . . . . .	9.696
Ferrous oxide . . . . .	36.859
Cupric oxide . . . . .	0.521
Nickelous oxide . . . . .	1.137
Magnesia . . . . .	6.871
Lime . . . . .	5.865
Potash . . . . .	0.207
Soda . . . . .	0.994

A specimen of the slag at Klefva had this composition:—<sup>3</sup>

Silica . . . . .	28.09
Alumina . . . . .	3.50
Ferrous oxide . . . . .	60.52
Cobaltous oxide	} . . . . . 1.44
Nickelous oxide	
Manganous oxide	
Sulphur . . . . .	0.58

<sup>1</sup> Schweder, *loc. cit.*

<sup>2</sup> Schnabel, *loc. cit.*

<sup>3</sup> Kerl, *Metallhüttenkunde*, p. 543.



This slag is added to the ore in ore-smelting to recover the nickel contained in it.

The iron sows have a similar composition to those formed in ore smelting. One at the Ringeriges works contained 20 per cent. nickel and 1.5 per cent. copper. These are put in with the ore in ore smelting, or worked up on the refining hearths.

At Klefva, in Sweden,<sup>1</sup> the coarse matte was roasted in stalls. It contained before roasting from 3 to 4 per cent. of nickel; it was smelted in a blast furnace about 5 feet high, with one tuyere in the back wall. The product contained from 45 to 57 per cent. of nickel; the coke used was 25 per cent. of the roasted coarse matte: quartz was added to the charge.

At the Ringeriges nickel works in Norway the coarse matte contained from 5 to 6 per cent. of nickel. It was smelted in blast furnaces 6½ feet high, and gave a concentrated matte with from 10 to 12 per cent. nickel, and from 7 to 10 per cent. copper. The charge was:—

100 parts . . . . .	Roasted matte.
25 „ . . . . .	Slag.
6 to 7 „ . . . . .	Sand.
5 „ . . . . .	Lime.
22 „ . . . . .	Coke.

The campaigns of the furnace lasted only 8 to 10 days, owing to the formation of iron sows rich in nickel (19 or 20 per cent.). At Kragerö, in Norway,<sup>2</sup> the original matte contained from 3 to 4 per cent. of nickel; after roasting it was smelted in a blast furnace about 4 feet 3 inches high, 38 inches wide, and 25 inches deep. The concentrated product contained 30 per cent. of nickel and 15 per cent. of copper. This matte was roasted and then smelted in the same furnace, and was converted into a matte with 60 per cent. Ni, 30 per cent. Cu, and 10 per cent. S. This last was completely roasted, and smelted to copper-nickel.

At the Sesia works at Varallo,<sup>3</sup> Piedmont, the raw matte contained 7 per cent. of nickel and cobalt; it was smelted in a blast furnace with the addition of 42 per cent. quartz, and the product was a matte with from 28 to 32 per cent. Ni, from 48 to 52 per cent. Fe, and 20 per cent. S. The daily output was 8.5 tons; 100 parts coarse matte gave 12 parts concentrated. To get 100 parts of the latter 17.5 parts of coke were used (dimensions of furnace not given).

<sup>1</sup> Balling, *loc. cit.*

<sup>2</sup> Dingler, vol. 229, p. 376.

<sup>3</sup> Badoureaux, *loc. cit.*

At the Isabella works in Dillenburg the original matte contained from 13 to 19 per cent. of nickel, and was roasted in reverberatories. It was smelted in blast furnaces to a concentrated matte, with from 28 to 30 per cent. Ni, and from 34 to 49 per cent. Cu. The furnaces were low blast furnaces, with one tuyere in the back wall, 5 feet high, 2 feet 4 inches wide and deep, arranged as "*Brillensfen*." The blast was 1·6 inches mercury. The campaigns lasted from 14 days to 3 weeks. From 100 parts coarse matte 32 parts concentrated matte used to be obtained. In 24 hours 1·25 tons of the roasted matte was put through. The quantity of coke is 55 per cent. of coarse matte; this is very high, and is caused by the low furnace.

#### *Smelting Roasted Matte in Reverberatory Furnaces*

These reverberatory furnaces are arranged just as those for the concentration of copper matte after the English method. To the roasted matte there is added a certain quantity of quartz, or glass, to slag the iron. The iron is partly slagged by the action of the quartz lining of the hearth.

The chemical changes in the smelting of the roasted matte, already referred to, are as follows. Ferric oxide is reduced to ferrous oxide by the undecomposed sulphide of iron present; this passes into the slag, and sulphur dioxide is formed; a further quantity of sulphide of iron is changed to ferrous oxide by the nickel and copper oxides, and also slagged, the oxides of these metals meanwhile becoming sulphides; further copper oxide and undecomposed copper sulphide give metallic copper and sulphur dioxide. This copper is reconverted into sulphide at the expense of some iron sulphide. The iron thus separated is partly taken up by the matte, partly act upon a corresponding amount of ferric oxide, giving more ferrous oxide to be slagged. There is no action between nickel oxide and sulphide. The various metallic sulphides unite to form the concentrated matte.

This method of concentration was formerly used at Sagmyrna, in Sweden, where the matte, containing from 13 to 14 per cent. of nickel, was first treated with dilute sulphuric acid to separate some of the iron; then roasted, and smelted in reverberatories with a quartz flux, giving a matte of 35 per cent. Ni, 40 per cent. Cu and 0·4 per cent. Fe.

#### *The Oxidation of Coarse Matte in Reverberatory Furnaces*

This is done in the same manner as the oxidising of copper matte in England. The unroasted matte is charged in a reverberatory furnace on a sand bed, and first subjected to a partial roasting, which removes

part of the sulphur and oxidises the iron; then the temperature is raised and the whole smelted with the addition of sand. The iron passes into the slag, and the nickel and copper present form a matte. The process is finished when samples from the furnace show that the greater part of the iron has been removed. It lasts about 8 hours. In England a furnace produced 2 tons of matte daily, with consumption of 2 tons of coal. Matte was obtained with only from  $2\frac{1}{2}$  to 3 per cent. of iron. The slag contained from 2 to  $2\frac{1}{2}$  per cent. of nickel. This was added to first ore-smeltings. By the repetition of the oxidation (which may be looked upon as the refining of the matte) the proportion of iron was brought down to 0.5 or 0.75 per cent.<sup>1</sup>

### β. THE REFINING OF THE COARSE MATTE OR THE CONCENTRATED MATTE

The refining of the matte can be effected by an oxidising roasting followed by a reducing smelting, or by an oxidising fusion of the matte. In both cases the iron is converted into ferrous oxide and slagged off. The former method, except in special cases, is dearer and more lengthy, and yields a less pure matte than the oxidising smelting method. At the present day the converter process is most frequently used for the removal of iron from matte.

The smaller the quantity of iron to be removed from the matte, the quicker and the less attended by loss is the oxidising fusion. Samples with less than 13 per cent. of nickel are rarely subjected to this process, and, unless great loss of nickel were to occur in the slag, these would give a matte still containing an appreciable quantity of iron, which would necessitate a second purification.

Roasting of the matte followed by smelting in shaft furnaces is used at the works of the Orford Copper Co., at Copper Cliff.<sup>2</sup> The nickel copper matte is prepared at the works of the Canadian Copper Co. at Sudbury, and sent for treatment to Copper Cliff. The roasting takes place in Brown furnaces as in the case of copper ores (vol. i. p. 98); the smelting in Orford shaft furnaces such as are used for copper ores (vol. i. p. 134). An Orford furnace puts through 100 tons of roasted matte in 24 hours, and produces a matte containing 80 per cent. of nickel and copper.

The plant for the oxidising fusion consists of hearths, converters or reverberatory furnaces. In hearths only small quantities of matte can be worked. The use of them renders a large consumption of

<sup>1</sup> Levat, *Ann. des Mines*, 1892, Bk. 2. pp. 141-244.

<sup>2</sup> *The Min. Ind.*, 1902, p. 495.

fuel and labour necessary. They have been used in Scandinavia and on the Continent, but have fallen into disuse owing to these drawbacks.

Converters permit of the working of large quantities of matte in the shortest time, and need only a very small quantity of fuel to fuse the matte (if this is not run directly into the converters in the liquid state from the furnaces in which it is produced), and, further, they ensure a more complete separation of arsenic and antimony than hearths and reverberatory furnaces. But they demand a blast with high pressure, and much fire-proof material for lining and renewing linings, whilst, during the operation, large quantities of sulphur dioxide are set free, which it is most difficult to prevent being noxious.

In spite of these objections they are preferred to reverberatory furnaces, wherever power is cheap, impure mattes have to be treated, and fuel is dear whilst refractory materials are cheap. They are used with good result at Sudbury, in Canada, and on the Continent.

Reverberatory furnaces can be managed more cheaply than hearths, and use raw fuel. The gases produced are comparatively poor in sulphur dioxide, and can be rendered harmless by passing into high chimneys. They are used where converters are not convenient from the noxious nature of their gases, or from not being adapted for small production; and where coal is very cheap. They are specially used in England.

The chemical changes in these various arrangements are the same, only they take place more rapidly in the converters than in the other forms.

The iron is converted into ferrous oxide by the oxygen of the air, and slagged by the silica of the furnace lining, or by siliceous matters added. Besides the iron a certain amount of nickel and of copper is oxidised, to the lower oxide in each case. Nickel monoxide with iron sulphide forms nickel sulphide and ferrous oxide. Cuprous oxide and copper sulphide form copper and sulphur dioxide, cuprous oxide and iron sulphide form copper sulphide, iron, ferrous oxide and sulphur dioxide. Separated copper takes sulphur from any iron sulphide remaining, and sets iron free, which passes into the matte.

Finally there results a matte of nickel and copper sulphides with less than one per cent. of iron.

#### *Refining of the Matte in Hearths*

This process was used formerly at Dillenburg and Gladenbach and in Norway and Sweden. Although now only of historical interest, a description of it may not be out of place.

The hearth is constructed exactly like the small refining hearth used for copper.<sup>1</sup> It consists of a cavity, hollowed in powdered quartz or sandstone, approximately hemispherical in shape, and over it is a chimney-hood. It contains according to size from  $1\frac{1}{2}$  to 5 cwts. of matte. In front of the hearth there is generally a small slag hearth, in which the slag from the former collects. The nickel-copper matte is either run off by a tap-hole in the deepest part of the hearth into a cavity in front, or else taken out of the hearth after cooling. There is one tuyere in the back wall of the hearth; it has an inclination of from  $22^\circ$  to  $32^\circ$ .

At the Isabella works the hearth of powdered sandstone was about  $14\frac{1}{2}$  inches in diameter,  $8\frac{1}{2}$  inches deep.<sup>2</sup> The charge was 187 lbs. The pressure was 1.2 inches mercury.

After the hearth was sufficiently dried by wood charcoal, the concentrated matte was melted with coke. After the lapse of  $1\frac{1}{2}$  hours the melting was complete. The fuel was then removed, and the slag floating on the surface of the matte blown cold and removed. Again fuel was piled up, and the oxidising blast used until a certain quantity of slag had collected, when it was again removed in the same way. The indication that iron was wholly removed from the matte was the appearance of an enamel-like lustre in the solidified slag: this generally appeared  $\frac{3}{4}$  hour after complete fusion. The working of one charge lasted  $2\frac{1}{2}$  hours. After the stoppage of the blast the nickel-copper matte was run into a cavity, lined with brasque, in the floor of the works, whereby it received the form of a slab 4 feet 3 inches long, 1 foot broad, and 2 inches thick. On the average  $13\frac{1}{2}$  cwts. of matte were blown in 24 hours. Out of 100 parts concentrated matte (with from 28 to 32 per cent. Ni and from 34 to 49 per cent. Cu) there were obtained 62 parts nickel-copper matte with from 39 to 42 per cent. Ni and from 40 to 42 per cent. Cu. For 100 parts of this latter, 72 of coke were required, and two men worked one hearth. The approximate composition of the nickel-copper matte may be seen from the following analyses by Fresenius:—

	I.		II.		III.
Cu . . . . .	42.81	. .	44.70	. .	40.72
Ni . . . . .	40.97	. .	39.68	. .	42.38
Co . . . . .	0.26	. .	0.64	. .	0.78
Fe . . . . .	0.23	. .	0.20	. .	0.48
Sb . . . . .	0.04	. .	0.90	. .	1.22
As . . . . .	0.16	. .	0.07	. .	0.04
S . . . . .	15.19	. .	13.55	. .	13.95
Residual matter . .	0.04	. .	0.02	. .	0.14

<sup>1</sup> Vol. i. p. 248.

<sup>2</sup> Schnabel, *loc. cit.*

This matte consisted of a mixture of metallic sulphides and metals, the latter including arsenic and antimony. It may be seen that the iron is reduced to a mere fraction per cent. It is hardly wise to attempt to remove this last trace, as a considerable quantity of nickel would thus be slagged off.

Further, arsenic and antimony remain in appreciable proportion in this matte. The refining slag contains nickel, partly chemically combined, partly mixed mechanically, on account of its high specific gravity.

The composition of such a slag at the Aurora Works at Gladenbach, where refining is carried on in the same way as at Dillenburg, is shown by the following analysis by Ebermayer:—

SiO <sub>2</sub>	36.291
Al <sub>2</sub> O <sub>3</sub>	10.710
FeO	48.690
CuO	1.074
NiO	2.142
CoO	0.262
MgO	0.309
CaO	0.680
Alkali	Traces.

At the Isabella Works the loss of metal in refining was 19 per cent. of copper and 4.9 per cent. of nickel. These metals were for the most part recovered, inasmuch as the slag was added in smelting ore.

At Klefva,<sup>1</sup> the hearth, made of quartz-sand, took a charge of about 5½ cwts. The tuyere had an inclination of 32°. To slag the iron-quartzose sand was thrown from time to time on to the molten charge. Wood charcoal was used as fuel. The refined matte, known as *Garstein*, had the following composition:—

Ni	61.06
Cu	30.73
S	7.79
Fe	0.42

At the Ringeriges Works,<sup>2</sup> a poor matte containing only from 10 to 12 per cent. of nickel and from 7 to 10 per cent. of copper was treated in the hearth. The matte resulting contained so much iron that it had to undergo further refining, which was carried on in a reverberatory furnace. The matte refined on the hearth contained:—

Ni	from 40 to 50 per cent.
Cu	20 „ 30 „
Fe	6 „ 10 „
S	20 „ 22 „

<sup>1</sup> Balling, *loc. cit.*

<sup>2</sup> Schweder, *loc. cit.*

*Refining of Matte in Reverberatory Furnaces*

The reverberatory furnaces for this purpose are constructed like those used in England for refining copper matte. The hearth is made of quartz. Quartz is added to slag the iron; heavy spar may also be added.

Silica reacts with barium sulphate to form barium silicate and sulphur trioxide, which latter is decomposed into the dioxide and oxygen.<sup>1</sup> Oxygen thus formed seems to have a specially marked action on iron sulphide. Since oxidation in a reverberatory furnace is less strong than in hearth furnaces and converters, there is frequently obtained a matte with 2.5 to 3 per cent. iron; in which case the process is repeated. Also arsenic and antimony are not so easily got rid of as they are in hearths, and much less easily than in converters.

The process is generally so arranged that there is at first a somewhat low temperature, as in the roasting fusion of copper matte, so that a sort of roasting of the matte takes place; after the addition of quartz sand, the temperature is raised.

The process is used in England and on the Continent. In England,<sup>2</sup> it is carried on in two operations; the first has already been spoken of under concentration of coarse matte, and yields a concentrated matte with from 2.5 to 3 per cent. of iron. The second operation (refining proper) is conducted exactly like the first (after the principle of the roasting fusion of copper matte), and yields a matte with from 0.5 to 0.75 per cent. of iron. The proportion of sulphur in the refined material must be at least 16 per cent., in order that it may be readily crushed down to the size necessary for the later dead roasting. The length of each operation is about 8 hours. During one day 2 tons of matte are worked up in the furnace, consuming an equal weight of coal. The slag which holds from 2 to 2½ per cent. of nickel is added in a first smelting operation.

At the Ringeriges Works, a matte which was at one time refined in reverberatory furnaces after having been purified by a blast, contained from 40 to 50 per cent. Ni, from 20 to 30 per cent. Cu, and from 6 to 10 per cent. Fe. To every 100 parts of this *Garstein* were added from 45 to 60 parts heavy spar, and from 20 to 30 parts sand. The firing was continued until the evolution of gases, chiefly sulphur dioxide, was finished. Then the slag was drawn off, and the refined matte tapped.

According to Wagner, it is possible to obtain a matte almost free from iron by smelting matte already purified by the blast with a

<sup>1</sup> Schweder, *loc. cit.*<sup>2</sup> Levat, *loc. cit.*

mixture of saltpetre and soda, either in crucibles or in reverberatory furnaces. A matte containing 25.32 per cent. Ni, 37.65 per cent. Cu, 10.58 per cent. Fe, and 26.45 S, yielded, when smelted with 15 per cent. mixed saltpetre and soda, a matte with 40.93 per cent. Ni, 58.64 per cent. Cu, 0.25 per cent. Fe, and 0.18 per cent. S. This method appears not to have come into use, for economic reasons.

### *Refining of Matte in Converters*

The converters are constructed like those for purifying copper-matte by the blast,<sup>1</sup> and, like them, have quartz linings. They are made like Bessemer converters, and also in the form of cylinders which can be rotated. The openings of the tuyeres at the sides must lie at a certain distance above the bottom. If the blast entered through the bottom of the converter, the nickel-copper matte collected there would soon be solidified. The matte is run directly into the converter out of the furnace in which it was produced, or else melted beforehand in a cupola furnace. The charge in the converter is from 1 to 6 tons of matte; the pressure up to 16 in. mercury. During the blow quartz-sand is added, to slag the iron and save the lining. The length of the blow varies, according to the content of iron, from 25 minutes to 1½ hours. At some works several charges are blown, one after the other, so that 3 to 4 hours may be taken from the beginning of the first blow to the pouring of the second or third charge.

With matte containing 36 per cent. of iron the time of the blow is 1 hour 20 minutes (at the works near Havre). When the proportion of iron has gone down to 0.5 per cent., the blast is stopped and the matte poured. The slag produced in this process is pasty, and contains from 2 to 15 per cent. of nickel, as well as 2 per cent. of copper, partly as silicates, partly enclosed mechanically. This is returned to the ore-smelting process.

At Sudbury the coarse matte treated in converters contains from 16 to 25 per cent. of nickel, from 20 to 27 per cent. of copper, and from 25 to 35 per cent. of iron. The matte should contain a certain amount of sulphur (16 per cent.) in order that it may be readily broken up for the ensuing roasting.

Attempts to separate metallic nickel by further application of the blast to the matte after the iron has been removed have been unsuccessful, because nickel, up to a certain stage, is more easily oxidised than sulphur, and because the heat set free by the oxida-

<sup>1</sup> Vol. i. p. 214.



tion of the sulphur is not sufficient to fuse and to keep fused the nickel with its high melting point.

In illustration of the Bessemer method we may quote the Canadian Copper Company's works at Sudbury, the works at Havre (France),<sup>1</sup> and of the Ludwig Mond Co. at Victoria. The plant of the first consists of four converters, of which one is always in operation, while a second is being given a new lining, the third cools and the fourth stands ready to start. In this arrangement 25 tons matte, which has been fused in cupola furnaces, is treated in 24 hours, and yields 15 tons refined matte. The iron is almost completely removed, while the proportion of nickel is increased to 40 per cent., and that of copper to 45 per cent. Sulphur is removed, except 5 to 15 per cent. The refined matte is tapped out of the converter and cast into square slabs about 3 inches thick and 3 feet in the side.

A converter holding 1·5 tons of matte at the beginning and 3 tons later as the lining gets eaten away is started with a blast pressure of half an atmosphere. Straightway begins a lively shower of sparks which lasts 6 to 10 minutes and may become so violent that the blast pressure has to be reduced by a half. If the temperature rises too high, cold matte is added. After the sparking ceases, a flame and a white smoke appear. The pressure is now raised to 0·8 atmosphere. As the temperature rises the flame changes in colour from red through blue to green. The process is at an end when the smoke disappears and the flame becomes clear. The blast is now stopped, the converter tipped after the matte and slag have separated, and the contents are poured into separate pots. Normally the slag does not contain more than 2 per cent. of copper and 3·5 per cent. of nickel. The average composition of the refined matte is

Cu . . . . .	43·36 per cent.
Ni . . . . .	39·96    "
Fe . . . . .	0·3       "
S . . . . .	13·76     "

It also contains 7 oz. of silver per ton, 0·1 to 0·2 oz. of gold, and 0·5 oz. of platinum. The slag contains:—

FeO . . . . .	67 per cent.	Cu . . . . .	1·0 per cent.
SiO <sub>2</sub> . . . . .	28       "	Ni . . . . .	1·7       "
		S . . . . .	0·5       "

At Victoria, Sudbury,<sup>2</sup> there are converters holding 6 tons of matte. They are in the form of movable cylinders, 7 feet long and

<sup>1</sup> T. Ulke, *The Min. Ind.*, 1894, p. 460.

<sup>2</sup> *Ibid.*, 1902, p. 495.

6 feet 8 inches in diameter; the wind-chest is 6 feet long and 1 foot high and there are 11 tuyeres. The matte which contains 30 to 50 per cent. of nickel and copper is charged into the converter from the ore-hearth of the shaft furnaces. The tuyeres are cleaned from time to time with iron bars during the first blow, which lasts 35 to 40 minutes; the converter is then turned and the slag poured. It is now brought into the upright position, blown again for 40 minutes, the slag poured and the matte run into a ladle carried by a travelling crane, from which it is cast into plates. If the quantity of matte is small, it is allowed to remain in the converter, and another charge added. This process is sometimes repeated and the matte from the three charges poured. The length of operation in these cases is from 3 to 4 hours. The plates weigh 500 lbs. After 4 to 8 charges have been put through, the converter is relined. The average composition of the converter matte is:—

Ni . . . . .	37·78 per cent.
Cu . . . . .	41·40 „
Fe . . . . .	0·65 „
S . . . . .	18·37 „
SiO <sub>2</sub> . . . . .	0·19 „

The slags contain 1·5 to 2 per cent. of nickel and 1·5 of copper. They are added to ore-smelting charges. The composition of the slag at the end of the process is given by Paris<sup>1</sup> as follows:—

Ni . . . . .	18·6 per cent.
Cu . . . . .	4·0 „
Fe . . . . .	16·9 „
SiO <sub>2</sub> . . . . .	49·0 „

At the Havre works<sup>2</sup> the converter holds only 1 ton. The blast pressure is 16 in. of mercury. Quartz sand is added, as soon as the temperature is high enough, to slag the iron. If the content of iron in the matte does not exceed 36 per cent., the operation is over in 80 minutes. If the percentage of iron is larger, it is necessary to tap out the iron slag first formed at the end of 25 minutes, and then continue the blow with the addition of more sand. As soon as the oxidation of nickel begins, the operation is stopped. The refined matte contains 0·5 per cent. of iron. The slag is difficultly fusible and contains 14 to 15 per cent. of nickel, chiefly in mechanically enclosed portions of matte. Part of this latter can be removed from

<sup>1</sup> *The Min. Ind.*, 1894, p. 466.

<sup>2</sup> T. Ulke, *ibid.*, 1894, p. 466.

the bottom of the slag-pots in metallic bottoms. The slag is returned to the ore-smelting.

Converters with basic lining have been proposed by Manhés,<sup>1</sup> but nothing is known about the application of these.

#### c. THE CONVERSION OF REFINED NICKEL MATTE INTO CRUDE NICKEL

This conversion consists of a roasting to convert nickel sulphide into oxide, and a subsequent reduction of the nickel oxide to nickel.

##### *Dead Roasting of the Matte*

This takes place in reverberatory furnaces in two stages. In the first the sulphur is brought down to 1 per cent. and in the second it is entirely removed, or nearly so.

According to Levat<sup>2</sup> the first roasting is carried out in a long-bedded calciner 33 feet long by 8 feet wide, with four working doors on one long side. The matte crushed in rolls is charged into the furnace 16 cwt. at a time, and spread out on the bed 2 inches thick. At first the temperature is kept at a dull red to prevent sintering, it is then raised gradually until it reaches a bright red at the end of the operation. The roasted product is withdrawn at the fire-bridge. The roasting lasts 8 hours and 36 cwt. of matte are put through in 24 hours, with a fuel consumption of 2 tons of coal. Three men are needed to attend the furnace.

The roasted matte contains still 1 per cent. of sulphur in the form of basic sulphates and undecomposed sulphides. It is ground as finely as possible, sieved, and roasted again in quantities of 10 cwt. in a calciner as wide as the first but much shorter. After 6 hours heating to a bright red the matte is roasted sweet; the coal-consumption is 3 tons per 24 hours, and the labour of two men is required. The oxide of nickel is greenish-grey, and should not contain more than 0.004 per cent. of sulphur.

##### *The Reduction of Nickel Monoxide to Nickel*

Nickel does not melt at the temperature of reduction of its oxide, so that it can be prepared in a powdery or spongy condition, or molten. If the spongy form be desired, the reduction takes place in tubes, retorts or muffles; if in the form of cubes, then the oxide is made into a stiff paste with meal, syrup or raw sugar, moulded into

<sup>1</sup> Ger. Pat., No. 80,467.

<sup>2</sup> *Ann. des Mines*, 1892, Livre 2, pp. 141-244.

cakes and dried, and these then cut into cubes and reduced with charcoal. If the metal is wanted as a powder, the oxide is mixed with charcoal and reduced. The crucibles used are made of graphite.

The reduction of the oxide in retorts of fire-clay is described by Künzel,<sup>1</sup> and has been carried out at Val Benoit, near Liège. The retorts are open at both ends, and have a width of 8 inches. They are placed in rows of 6, in a furnace of similar construction to the French one for liquation of antimony at Malbosc. The charging is done through openings in the arch of the furnace, to which openings correspond similar ones in the bed. Under these latter are tubes of iron plate, about 5 feet long, forming continuations of the clay retorts, and upon these iron pipes the clay ones rest. The iron pipes serve for the cooling of the nickel cubes formed in the retort, and they themselves rest, with three-quarters of their periphery, on an iron plate. At the beginning of the operation the retorts are filled to a certain height with small coal, upon which the cubes of oxide of nickel are charged. From time to time part of the contents of the coolers are removed through an opening in the lower part of the tubes. In this way the grains slide down the heated clay retorts, and finally are delivered into the coolers in the metallic condition. The removal of the cubes takes place every three-quarters of an hour or hour. At Val Benoit, in 24 hours, 10 or 12 cwts. of nickel are produced in a furnace with 6 retorts, with a consumption of 18 to 20 cwts. of coal.

At the Silesian nickel works, Frankenstein,<sup>2</sup> the tubes are 8 inches in diameter and 30 inches high. They stand in two rows of ten each in a gas heated furnace with generators. The furnace is 13 feet long and 33 feet broad and the reduction lasts 3 hours.

Very recently, according to Knut Styffe,<sup>3</sup> furnaces with muffles have been brought into use for preparing spongy nickel. A furnace of this kind holds 12 muffles, which are placed in two rows one above the other, and fired by a single fireplace. The furnace has working doors for each of these rows on opposite sides. The reduction lasts 4 hours. The temperature is raised to 1200°, in consequence of which the reduced nickel sinters into sufficiently solid pieces.

Levat<sup>4</sup> communicates an arrangement of a furnace with a single muffle, illustrated in Fig. 460. The furnace is 11½ feet long and 6 feet wide. The muffle has an opening on the short side, and is there

<sup>1</sup> Kerl, *Metallhüttenkunde*, p. 553.

<sup>2</sup> *Zeits. f. Berg-, Hütten- u. Salinenwesen im Preuss. Staate*, 1902, p. 816.

<sup>3</sup> *Oesterr. Zeitsch.*, 1894, p. 324.

<sup>4</sup> *Loc. cit.*

closed during the operation by doors (*k k*). These doors are counterpoised and protected within by fireproof linings. Gas fuel is used; *l, l*, are the flues through which the flames play round the muffle. The oxide to be reduced is charged into iron vessels *m, m*, which are introduced at the side of the furnace opposite the generator, and gradually pushed forward until they are drawn out at the hottest place. Each crucible remains 24 hours in the furnace.

To obtain the nickel in a molten condition, a little flux is added to the mixture for reduction and the reduction carried out at a temperature above the melting point of the metal. The molten metal can be cast in any desired form. If the nickel reduced alone is to

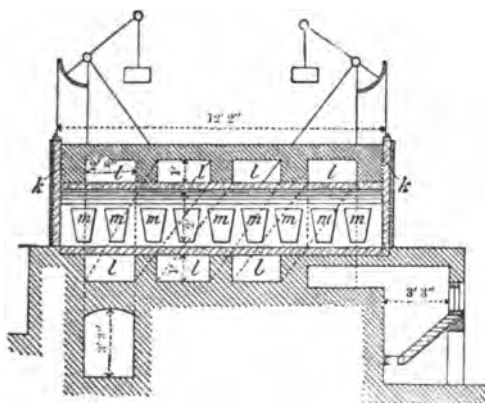


FIG. 460.

sinter properly, it must be heated in the crucibles to a temperature of  $1100^{\circ}$ – $1200^{\circ}$  for at the very least 4 hours.

The production of molten nickel from the monoxide is carried out, as described below, at the Orford Copper Company's works, Bergen Point, New York Harbour.

#### *d.* THE CONVERSION OF REFINED NICKEL COPPER MATTE INTO RAW NICKEL

Two dry methods have been used so far for this purpose, viz., the Orford process and the Mond process; none of the other proposals has reached the practical stage.

The Orford process consists in removing the copper and the little residual iron from nickel-copper matte, by repeatedly smelting it with sodium sulphate and coal. The nickel sulphide remaining after

this treatment is roasted to oxide and then reduced to metal in the ordinary way.

In the Mond process the matte is roasted, the copper partly removed, and then reduced to a nickel-copper alloy. By the action of carbon monoxide upon this, the nickel is converted into the gaseous nickel carbonyl, and this on heating yields up its nickel. Both processes are kept secret, and their economic results cannot be judged.

### *The Orford Process*

The method is used at the Orford Copper Company's works at Constable Hook, New Jersey, near New York. The operation has been devised and is practically carried out by John Thomsen, director of the above company, and Charles Bartlett.<sup>1</sup> Since it is kept secret, only incomplete accounts have become public. According to these, coarse matte or preferably concentrated matte is smelted with sodium sulphate and coal in a small blast furnace, where the sulphate is reduced to sodium sulphide. The sodium sulphide combines for the greater part with sulphides of copper and iron and converts any metallic copper and iron formed in the operation into sulphides, caustic soda being produced thereby. The sulphides of copper, iron and sodium, and the caustic soda form a readily fusible mixture, which dissolves part of the nickel sulphide. The greater part of the nickel sulphide, however, separates out along with a little sulphide of iron and copper, and settles to the bottom owing to its greater density. The products are tapped out into a receiver and allowed to cool. They separate into two layers, "the tops" and "bottoms," which can be readily separated after cooling. The tops consist of sodium sulphide, caustic soda, iron and copper sulphides and a little nickel sulphide; the bottoms consist chiefly of nickel sulphide, with small quantities of the other sulphides and caustic soda.

The tops are digested repeatedly with copper chloride liquor, obtained by leaching concentrated tops which have undergone a chloridising roasting, and they are then smelted with tops (obtained in the concentration of bottoms) which have been similarly treated, fresh copper-nickel matte being added; the products are concentrated tops and bottoms.

The bottoms from the first smelting process are smelted with sodium sulphate and coke and the bottoms obtained in concentrating tops, the products being tops with but little nickel, and concentrated

<sup>1</sup> *Mineral Industry*, 1892, p. 357. John L. Thomsen, American patent, No. 489,882, January 10, 1893. German patent, No. 91,288.

bottoms, rich in nickel and poor in copper. These tops are worked, owing to their high copper content, along with the tops from the first smelting process as described above.

The concentrated tops are first leached with water in order to bring the sodium sulphide into solution, and the residue, consisting chiefly of copper sulphide, is treated for copper. The sodium sulphide liquor is evaporated, and the solid body left is added to the matte-smelting charges. The concentrated bottoms form a nickel matte containing only very small quantities of copper.

The treatment of the nickel matte for nickel is the same as described above, viz., the matte is roasted dead and the resulting oxide is reduced by carbon.

In many cases nickel oxide itself is sent into commerce, being used in the preparation of nickel-steel. The nickel matte produced in the Orford process is subjected to a chloridising roasting in order to convert its copper into chloride. This is leached out and the solution used partly for digesting tops and partly for precipitation by iron. Any of the platinum metals present in the matte become chlorinated in the process and pass into the solution. Nickel monoxide is left after leaching.

The composition of nickel oxide from Canadian matte is given below :—

	Ordinary oxide.	Better quality.
NiO(+CoO)	97.5	98.74
CuO	0.4	0.30
Fe <sub>2</sub> O <sub>3</sub>	1.5	0.70
As	0.3	0.04
S	0.03	0.02
SiO <sub>2</sub>	0.3	0.20

According to v. Ehrenwerth,<sup>1</sup> there are used for reduction and fusion, at Bergen Point, graphite crucibles 18 inches high and 14 inches wide, in each of which 75 lbs. of nickel monoxide are placed. Wood charcoal is the reducing agent (16 per cent. by weight of the oxide); petroleum fuel is used. The plan of the furnace is shown in Figs. 461, 462. The furnace has three chambers each holding two crucibles, the furthest chamber always standing empty. The middle chamber gives the crucibles a preliminary heating, and the one nearest the fire serves to melt the reduced nickel. The petroleum flame passes through the various chambers in the direction indicated by the arrows, and finally reaches the chimney E. The petroleum runs first into the

<sup>1</sup> *Loc. cit.*, p. 550.

uppermost of three trays  $p$ , stretching the full width of the furnace, placed one under another. When the top one is full, the petroleum flows into the next below  $p'$ , and when that is full into the third  $p''$ . The petroleum that flows away from the lowest passes into a receiver outside the furnace. The air for the combustion enters through the channels  $S$ , and then passes in the direction indicated by the arrow, through a channel going under the furnace, for preliminary heating before entering the fireplace. Such a furnace can smelt three charges in 12 hours, and produces in this time 2400 lbs. nickel with an expenditure of 105 gallons of petroleum. The liquid nickel is poured into iron moulds and takes the form of bars. The material reduced is said to contain 90 per cent. nickel monoxide.

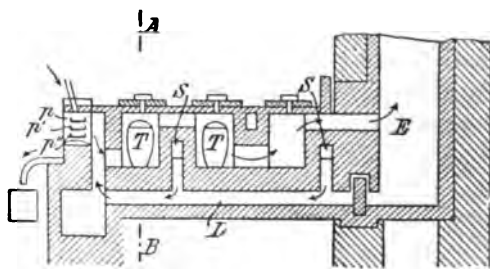


FIG. 461.

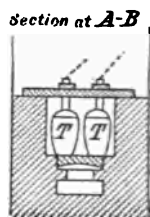


FIG. 462.

and the metal produced 96 to 98 per cent. nickel and 0.5 per cent iron.

A sample of commercial Canadian nickel gave the following analysis:—

Ni	98.74	Fe <sub>2</sub> O <sub>3</sub>	0.70
As	0.04	CaO	0.30
S	0.02	SiO <sub>2</sub>	0.20

### *The Mond Process*

This process,<sup>1</sup> which was devised in the year 1889 by Dr. Ludwig Mond, assisted by Dr. Carl Langer, consists in the reduction of nickel oxide to finely divided nickel by treatment with hydrogen, water gas or producer gas at 300° C.; in the conversion of this nickel into the volatile nickel carbonyl Ni[CO]<sub>4</sub> by the action of carbon monoxide at a temperature not exceeding 100° C., and in the decomposition of this nickel carbonyl at 180° C, into nickel and carbon monoxide. The

<sup>1</sup> Ger. Pat., Nos. 57,320, 95,417, 98,643. *The Eng. and Min. Jour.*, December 15, 1898, p. 784. *The Min. Ind.*, 1899, p. 526; *The Chem. News*, 78, 260; *Revue générale de Chimie pure et appliquée*, vol. ii. No. 4.



latter is then used for the treatment of fresh quantities of nickel. If the ores and metallurgical products which furnish the nickel contain the metal as sulphide, they are roasted to convert this into oxide. This method, which is in use at Smethwick near Birmingham, has only been applied so far to nickel-copper mattes containing little iron.

The raw material is refined nickel-copper matte from Sudbury in Canada. This matte is roasted dead to convert sulphides into oxides, leached with dilute sulphuric acid to remove most of the copper, and then treated with water-gas in a reduction tower, whereby metallic nickel and copper are formed. The resulting alloy is exposed to the action of carbon monoxide in a volatilising tower, or "volatiliser," and the nickel carbonyl so produced is drawn by a fan into a decomposition tower, where it is split up by heating into nickel and carbon monoxide; the latter is drawn off to the volatilising tower for further use. As the reduction and volatilisation of the nickel is far from complete in one operation, this process has to be repeated many times, the matte being withdrawn from the volatilising tower and charged into the reduction tower, whence it comes again to the volatilising tower, and so forth. It is not possible, however, to exhaust the matte, even by repeated reduction and volatilisation. After two-thirds of the nickel has been removed, the reaction becomes so slow owing to the presence of undecomposed sulphides, that the process is stopped, the matte roasted and leached again, and the product put through the same cycle of operations.

The dead-roasting of the matte takes place generally in rotating reverberatory furnaces. The roasted matte contains 25·27 per cent. of nickel, 41·87 per cent. of copper and about 2·13 per cent. of iron.<sup>1</sup> It is ground in ball mills, put through a sieve with 60 meshes to the linear inch, and then leached with dilute sulphuric acid in quantities of 3 cwts. at a time in lead-lined vats fitted with stirrers. The leaching liquor is made up of 200 lbs. of oil of vitriol and 120 gallons of the mother liquor left after the crystallisation of copper vitriol from a previous operation. The temperature is kept at 85° C. by blowing in steam. This treatment dissolves out chiefly the copper. Nickel and iron are soluble to some extent, and the solution becomes concentrated in these by repeated use. After leaching has gone on for half-an-hour, the liquor is drawn off into crystallising dishes, in which the copper sulphate crystallises out after 8 to 10 days. The residue after drying contains 52·5 per cent. of nickel, 20·6 per cent. of copper and 1·6 per cent. of iron. The copper sulphate contains 0·05 per cent. of

<sup>1</sup> Roberts-Austen, Inst. of Civil Eng., London, November 8, 1898. *The Min. Ind.*, 1899, p. 526.

iron and the same amount of nickel. It is dried in centrifugal machines and sent to the market, and the mother liquor is used in leaching fresh quantities of roasted matte.

When the mother liquor has become concentrated up to a given point with iron and nickel salts, it is evaporated to dryness, and the mixture of the sulphates of iron, copper and nickel is heated to convert it into oxide. The oxide mixture is then reduced along with the leached-out matte.

The reduction of the roasted and lixiviated matte is carried out at a temperature of  $250^{\circ}$  to  $300^{\circ}$  C., the nickel produced at this temperature being readily reactive with carbon monoxide at a temperature of  $50$  to  $60^{\circ}$  C. The nickel reduced from its oxide at  $400^{\circ}$  C., or above this temperature, is not so finely divided, so that the reaction with carbon monoxide is slower, and the volatilisation less complete.

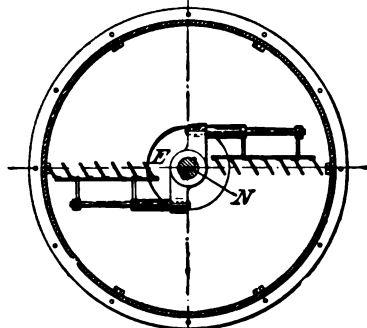
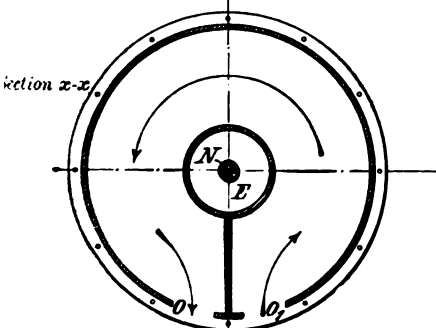
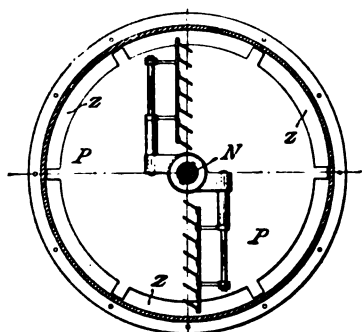
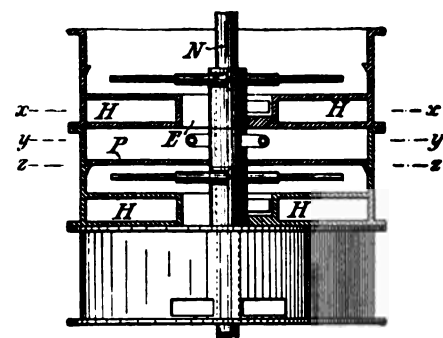
The reduction of nickel oxide to the metal, and the cooling of this to the temperature suitable for treatment with carbon monoxide, takes place in a reduction tower. This must be so constructed that the temperature in all parts can be easily regulated; it is made of separate short cylinders each of which can be heated or cooled from the outside. The construction of these component cylinders is shown in Figs. 463 to 466.<sup>1</sup> The bottom  $H$  of each cylinder is hollow and serves for the introduction of hot gases, cold air or water. This space is so divided by a partition (Fig. 464) that the heating and cooling agents entering at  $O_1$  must circulate in the direction shown by arrows, and discharge at  $O$ .

The opening  $O_1$  of each cylinder is connected by a pipe (with damper) to the hot and cold mains, and the opening  $O$  with the exhaust flues. The cylinders are placed so that the bottom of one forms the top of the next beneath it. The material to be treated is spread out by stirrers upon the floor of the cylinder. To enable this to be done there is a plate  $P$  (Fig. 465) in the upper part of each cylinder, fitting closely to the upright shaft  $N$ , though without interfering with the free motion of this. This plate has a smaller diameter than the cylinder, so that there is a space  $Z$  (same Fig.) between its outside edge and the cylinder wall. Rabble arms with teeth are fixed to the shaft  $N$  which passes through the middle of the tower, the teeth being so arranged that the material is moved from the centre to the periphery (Fig. 463), where it falls through the slot  $Z$  to the bottom of the cylinder. Here it is moved by a second stirrer from the periphery to the centre (Fig. 466), and falls through an opening  $E$  (not connected with the heating chamber) on to the plate  $P$  in the

<sup>1</sup> Ger. Pat., No. 95,417.

cylinder lying below it (Figs. 463 to 465). In this way the matte to be reduced falls through all the cylinders which make up the tower. Water-gas which is used for the reduction rises through the tower in the opposite direction.

The reduction tower at Smethwick is 25 feet high and made up of 14 cylinders. The floors of the 7 top cylinders are heated to  $250^{\circ}\text{C}$ . with producer gas, the 5 lowest cylinders are cooled by water. If the matte contains iron, the temperature must be kept as low as possible



FIGS. 463 and 464.

FIGS. 465 and 466.

to prevent the reduction of the oxide of iron to metal, and the formation of iron carbonyl in the volatilisation tower. If this happens the nickel will be contaminated with iron. Nickel produced from a matte containing 6 to 10 per cent. of iron should not contain more than 0.5 per cent. of iron. Should the matte contain more iron, the low temperature needful to prevent its reduction would result in an incomplete reduction of the nickel oxide. Matte with more than 10 per cent. of iron must therefore be freed by smelting from the greater part of it, before it can be submitted to the Mond process.

The water-gas used in the reduction is generated in producers by blowing steam over anthracite, and is collected in gasometers. The

gas leaving the reducing towers still contains 5 to 10 per cent. by volume of hydrogen. Part of it is used for preparing the carbon monoxide necessary for the volatilisation of the nickel, by passing it over glowing charcoal in a heated retort, after the water vapour has been removed by scrubbing. The carbon dioxide is thus reduced to monoxide, and the resulting gas, containing 80 per cent. of carbon monoxide, is collected in a gasometer.

The conversion of the nickel into the carbonyl compound is carried out in a volatilising tower or volatiliser at a temperature below 100° C. The best temperature for the formation of this compound is 50° C., since at that temperature the impurities (even cobalt) are not attacked. The volatilisers are arranged like the reduction towers, with the difference that there are no chambers in the bottoms of the component cylinders. There is no need for separate heating as the heat of the nickeliferous material from the reduction towers and of the carbon monoxide itself suffice to maintain the right temperature of 50 C.° The material to be treated is conveyed through the tower exactly as in the case of the reduction towers, and the carbon monoxide rises through it in the opposite direction.

The carbon monoxide is derived partly from the decomposition of nickel carbonyl and partly, as explained above, from the escaping gases from the reduction towers. According to former accounts it was generated by passing carbon dioxide over glowing coke, the carbon dioxide being produced by boiling potassium bicarbonate solutions, obtained by passing the gases from a boiler furnace into potash solution.

The volatile nickel carbonyl is drawn by a blower through a filter into the decomposition tower. After the carbon monoxide has acted some time upon the nickel, the reaction slackens. The residues are then reduced again in the reduction tower, and brought back to the volatiliser for further treatment. In this way the nickeliferous material is worked first in one tower and then in the other until 60 per cent. of the nickel has been volatilised, the time taken being from a week to a fortnight. The residue is then one third of the original matte, and contains 35·48 per cent. of nickel, 38·36 per cent. of copper and 4·58 per cent. of iron, chiefly in the form of undecomposed sulphides. It is treated like the original matte, and after repetition of the various processes, it contains only 20 per cent. of its original nickel content. The second residue contains 35·83 per cent. of nickel, 35·36 per cent. of copper and 7·82 per cent. of iron, and it weighs only about one-tenth of the original matte. There is no information in the literature of the subject about the further treatment of this. Presumably it is added to fresh matte.

The nickel carbonyl, after filtration to remove flue dust, is decomposed into nickel and carbon monoxide at  $180^{\circ}\text{C}$ . This was done formerly in empty chambers in which the nickel was precipitated in a loose spongy condition, hard to work up. At present the nickel is obtained in compact spherical masses, by leading the carbonyl over granulated metallic nickel in the form of small shot.

The construction of the decomposition tower is seen in Fig. 467. It is a jacketed cylinder with funnel-shaped bottom and the nickel carbonyl is led in through a central pipe reaching nearly to the bottom. *A* is the tower with its charge of nickel granulations, *B* is the central inlet tube for the carbonyl compound, deposition of nickel in this tube being prevented by cooling it with water which circulates in a smaller tube. In the jacket there are heating chambers *H* for the circulation of hot air, whereby the temperature of the tower is brought up to  $200^{\circ}\text{C}$ ., the decomposition temperature of the carbonyl. The nickel carbonyl enters the tower through holes in the pipe *B*, and passes through the shot, becoming decomposed thereby and the nickel precipitated. To prevent stoppages and caking of the mass, the shot is kept in constant slow motion by a screw *U* which is partly enclosed by a sieve *N*, so that the small shot fall through the sieve and are returned by a lift to the tower, while the larger grains which cannot pass the mesh collect in the chamber *G* and are discharged at intervals into waggons brought below. The larger grains are suitable for technical use. The carbon monoxide gas, after freeing from nickel, is drawn off through the pipe *M* and blown into the volatiliser.

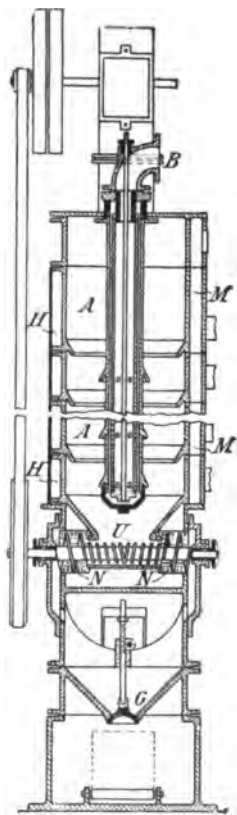


FIG. 467.

Two specimens of Mond nickel showed the following composition :

	I.	II.
Ni	99.82	99.43 per cent.
Fe	0.10	0.43 „
S	0.0068	0.0099 „
C	0.07	0.087 „
Insoluble Residue	—	0.026 „

Nothing is known of the economic results of the Mond process. The weak points in it seem to be: the need for keeping much nickeliferous material in circulation, dangers of explosion, loss of nickel and poisoning of the workmen by carbon monoxide when the apparatus becomes leaky. In 1902 a damaged plant was responsible for the poisoning of 20 workmen.<sup>1</sup>

*Other Methods for the Treatment of Refined Nickel-copper Matte.*

The process of Emmens consists in a chloridising roasting of the matte in presence of steam, extraction of the chlorides of copper and other metals with water, and smelting of the residue, consisting of nickel and iron oxides, with sodium sulphide, sand and charcoal. In this way a pure nickel matte is produced; this is roasted dead and the nickel oxide reduced to metallic nickel.<sup>2</sup>

This process is only possible of execution when the matte contains small quantities of copper; otherwise all the copper is not chlorinated. In the roasting, chlorides of nickel and iron are formed which are leached out with the copper; part of the copper is converted into cuprous chloride which is insoluble in water and must be extracted with hydrochloric acid or chloride solutions; and sulphates of copper, nickel and iron, all of which are soluble in water, are formed to some extent. The process has been used in America.

Hybinette and Ledoux<sup>3</sup> have proposed to separate nickel from its molten matte with manganese, manganese and copper combining more readily with sulphur under these conditions than nickel. At the first operation less manganese is added than is required to replace all the nickel; a mixture of nickel and its sulphide settles to the bottom and a layer of the sulphides of copper and manganese floats on the top of this: the latter is removed and more manganese added to the residue. This completes the separation of the nickel. The tops may be used for the extraction of copper and manganese. The manganese is added in the form of peroxide from which the metal may be obtained by reduction with carbon.

This method is said to have been used at the Balback works in Newark, though nothing is known as to its definite adoption.<sup>4</sup>

Removal of copper from nickel mattes by blowing in a converter

<sup>1</sup> *The Min. Ind.*, 1899, p. 487.

<sup>2</sup> *The Min. Ind.*, 1894, p. 463.

<sup>3</sup> U.S.A. Patent, March 16, 1897, No. 579,111.

<sup>4</sup> *The Min. Ind.*, 1896, p. 430.

<sup>5</sup> Von Ehrenwerth, *Das Berg- u. Hüttenwesen auf der Weltausstellung*, Chicago. Vienna, 1895.

(with lining of basic material or of coke) has been suggested, though it is not known whether the method has been carried out in practice. It is said that the iron is first slagged off, then the nickel, and the copper separates out lastly as metal. The nickel slags may be collected apart from the iron slags, and worked up for nickel in the dry or the wet way. The operation takes place in two periods, slags and fluxes being added to the matte charges. In the first period the iron is slagged and a copper nickel matte free from iron results; in the second period the nickel is slagged and metallic copper left behind.

#### c. THE CONVERSION OF REFINED NICKEL-COPPER MATTE INTO COPPER-NICKEL ALLOYS

##### ROASTING THE MATTE

It must be dead roasted. To this end it is powdered as finely as possible, and then twice roasted in a reverberatory furnace. Oxidising material, such as saltpetre, is frequently added in the second roasting. Long-bedded calciners, as also short hand-worked reverberatory furnaces, are used for this operation.

At Klefva, in Sweden,<sup>1</sup> one of the former kind, with sloping hearth, was used; it held four roasting charges, of  $2\frac{1}{2}$  cwt. each. At Gladenbach,<sup>2</sup> in Nassau-Hesse, a furnace was used with a rectangular hearth about 45 square feet in area, with a single working opening and two flues. The greatest height of the arch of the furnace above the bed was 14 inches: the charge was 4 cwt.

During the first roasting sulphur was removed down to 1 per cent. The roasted matte was pulverised, and then further roasted to remove the last portion of sulphur. The first roasting lasted 6 to 12 hours, the second 6 to 8 hours. According to Levat, the consumption of fuel for 1 ton of refined matte was  $\frac{5}{8}$  ton of coal in the first roasting, and  $1\frac{1}{2}$  tons in the second. The result of the roasting was a mixture of cupric oxide and nickel monoxide, which had a dark grey to black colour according to the proportion of copper.

At the Aurora works at Gladenbach<sup>3</sup> about 4 cwt. of pulverised matte was spread out on the hearth an inch or inch and a half deep, and roasted for 12 hours, with continuous raking through and occasional turning. To prevent sintering of the material the temperature was lowered at the beginning of the roasting, and not allowed

<sup>1</sup> Balling, *loc. cit.*

<sup>2</sup> Schnabel, *loc. cit.*

<sup>3</sup> Schnabel, *Preuss. Ministerialzeitschrift*, 1866, p. 137.

to rise above dull redness until the end, when it was brought to a bright redness. Sulphur was removed in this first roasting down to  $\frac{1}{2}$  per cent.

The product was powdered and then subjected to an 8 hours roasting in the same furnace with the addition of saltpetre and soda. At first the temperature was raised to a bright redness, but finally brought to a white heat to completely decompose the sulphates formed. During this second roasting arsenic and antimony were converted into arseniates and antimoniates by the saltpetre and soda, and these were removed by washing with water before further treatment.

At Klefva<sup>1</sup> the roasting was carried on in furnaces with inclined hearth. In these, four charges, each of  $2\frac{1}{2}$  cwt., were put through. Wood was used as fuel. In the first roasting, one charge ( $2\frac{1}{2}$  cwt.) was put through in about 4 hours; in the second roasting, in the space of about 8 hours.

At the Ringeriges works in Norway<sup>2</sup> sulphur was removed down to 2 or 4 per cent. in the first roasting. In the second, 10 per cent. by weight of calcined soda and 5 per cent. of saltpetre were added to the already roasted matte. The salts thus formed were leached out by water from the product.

According to Levat the refined matte is completely roasted in two operations in the newer works in England and on the Continent. During the first, sulphur is removed down to 1 per cent., in the second at the most only 0.004 per cent. remains. The first operation is carried on in a long-bedded calciner 33 feet long and 8 feet broad with four working doors in the long side. The matte, crushed between rolls, is put into the furnace in charges of about 16 cwt., and spread on the bed to a depth of 2 inches. The temperature at first is kept down to dull redness to avoid sintering, and raised to bright redness at the close of the operation. The product is drawn out at the firebridge. The length of the operation is about 6 hours for matte containing copper, and 8 hours if free from copper, as the nickelous sulphide is more difficult to decompose than copper sulphide. The quantity put through in 24 hours is  $2\frac{1}{2}$  tons for first charge, or 36 cwt. for second, with a fuel consumption of 2 tons of bituminous coal. The furnace is tended daily by three men.

The product, which contains about 1 per cent. sulphur due to the presence of undecomposed lower sulphides and basic salts, is crushed as fine as possible by rolls, sieved, and put for a second roasting into a furnace as wide as that described last, but much shorter. The

<sup>1</sup> Balling, *loc. cit.*

<sup>2</sup> Schweder, *loc. cit.*



charge is half a ton of the preceding product, which is completely roasted at a bright red heat in 6 hours. Every 24 hours 3 tons of coal are used. The furnace is tended by two men in a day. The oxide now resulting should not contain more than 0.004 per cent. sulphur. It is black if copper is present, and greenish-grey if it is not.

#### REDUCTION OF COMPLETELY ROASTED NICKEL-COPPER MATTE TO COPPER-NICKEL ALLOYS

The mixture of cupric and nickelous oxide is reduced to a copper nickel alloy. The process can be carried on, so that either an alloy without fusion is obtained in powder, dust or cubes, or so that the alloy is obtained fused.

Nickel monoxide is reduced at a strong red heat, without being fused at that temperature. Cupric oxide is reduced at a still lower temperature.

The formation of alloy in the form of powder or cubes takes place in muffles, in crucibles, or in tubes, while the production of fused alloy takes place in shaft furnaces.

To make the powder the oxides are mixed with powdered coal and pressed tight in graphite crucibles; to make cubes they are made into a stiff paste with viscid carbonaceous substances (syrup, meal, raw sugar) with the addition of water, made into flat cakes, and lastly divided into little cubes of 0.4 to 0.6 inch side. These are ignited with powdered charcoal in crucibles or tubes.

To make the fused alloy the oxides are smelted with charcoal in a little shaft furnace.

At Klefva<sup>1</sup> the oxides were reduced in the form of powder in graphite crucibles in quantities of about 19 lbs. The crucibles were heated for 12 hours in a wind furnace which held from 8 to 12 pots. The pulverised alloy, which was a commercial product, had the following composition:—

	I.	II.
Ni . . . . .	60.25	66.46
Cu . . . . .	38.85	32.33
Fe . . . . .	0.64	0.70
S . . . . .	—	0.08

At the Ringeriges works the moist oxides were mixed with raw sugar, made into cubes, dried, and placed in crucibles in layers with powdered charcoal, and kept at a white heat for 5 hours. The cubes obtained were emptied into an iron box, in which they were cooled,

<sup>1</sup> Balling, *loc. cit.*

then separated from the charcoal by sieving, and finally polished with water in a rotating drum.

At the Victoria works in Silesia<sup>1</sup> the oxides were made into a paste with wheat-meal, then spread out on a copper sheet, divided into cubes and dried. The cubes were placed in layers with charcoal in graphite pots, and these heated in a wind furnace with coke; for one pot yielding about 11 lbs. alloy, 13 to 15 lbs. of coke were needed.

The reduction of the oxide in a blast furnace was formerly carried on at the Aurora works at Gladenbach,<sup>2</sup> and also occasionally at Klefva. At the former place the blast furnace, arranged as a crucible furnace, was 2 feet high, 1 foot 4 inches deep, and 1 foot 6 inches wide. The sole consisted of a light brasque (4 to 5 parts by volume of wood charcoal, 1 of loam). The blast, at a pressure of  $1\frac{1}{4}$  inches mercury, was given by one tuyere in the back wall, with an average inclination of  $45^\circ$ . Wood charcoal was used for the reduction. As soon as a quantity between 175 and 220 lbs. of oxide was run down, the alloy and slag were tapped out into a little fore-hearth. After the solidified slag was removed from the alloy, the latter was taken off in discs and broken into pieces while still red-hot. Out of 100 parts oxide 35 to 38 parts alloy were obtained.

An easily fusible slag was formed by part of the oxides, the loam of the brasque, and the material of the furnace wall, which slag protected the alloy from being oxidised by the air of the blast. The slag contained considerable quantities of copper and nickel, and had also to be worked up separately for alloy. The loss of metal was 1.35 per cent. Ni and 8.22 per cent. Cu. Out of a refined matte which before roasting had the composition:—

Ni . . . . .	32.59 per cent.
Cu . . . . .	52.00 „
Fe . . . . .	0.41 „
S . . . . .	17.71 „
As+Sb . . . . .	0.11 „

an alloy was obtained containing:—

Cu . . . . .	59.5 per cent.
Ni . . . . .	39.95 „
Fe . . . . .	0.64 „

<sup>1</sup> *Berg- und Hütten. Zeitung*, 1877, p. 300; 1878, p. 245.

<sup>2</sup> Schnabel, *loc. cit.*

Out of an original matte which when unroasted had this composition:—

Ni and Co . . . . .	37·5	per cent.
Cu . . . . .	48·5	„
As and Sb . . . . .	Trace	„
S . . . . .	13·3	„

an alloy was obtained containing:—

Ni . . . . .	45·06	per cent.
Cu . . . . .	53·44	„

The dead-roasted nickel-copper matte from Canada is reduced with wood charcoal or gas, and an alloy obtained containing 50 per cent. of copper, 49 per cent. of nickel and small quantities of iron, silicon and carbon. This is sent to the German-silver works. A special alloy composed of parts of 4 copper to 1 part of nickel is made for cartridge shells.

## 2. EXTRACTION OF NICKEL FROM THE SILICATE (GARNIERITE)

This New Caledonian ore is a hydrated silicate of variable composition, the constituents lying between the following limits:—

NiO . . . . .	9 to 17	per cent.
SiO <sub>2</sub> . . . . .	41 to 46	„
Fe <sub>2</sub> O <sub>3</sub> . . . . .	5 to 14	„
Al <sub>2</sub> O <sub>3</sub> . . . . .	1 to 7	„
MgO . . . . .	6 to 9	„
H <sub>2</sub> O . . . . .	8 to 16	„

The nickel content of the garnierite which is smelted has of late decreased to between 7 and 8 per cent. At present it is treated only in Europe (Glasgow, Birmingham, Havre, Iserlohn). An earlier method of treatment was carried on in the neighbourhood of Noumea in New Caledonia, and consisted in smelting the ore in a blast furnace with coke and fluxes, producing a nickel-iron alloy, which was sent to Europe to be converted into pure nickel.

At Noumea the pulverised ore was mixed with fluorspar, cryolite, soda, manganese ores and powdered coal, and made into bricks with tar. It was then smelted with coke in a furnace 26 feet high, with a blast heated to 400° and at a pressure of 5 inches of mercury; the product was iron-nickel alloy. Limestone was added to combine with

the sulphur in the coke, half a ton being needed per ton of ore. If the ore contained too little iron, other ores rich in iron were added. On the average from 1,000 parts of ore 112 parts ferro-nickel were obtained with a consumption of 400 parts coke.

The composition of this ferro-nickel is seen from these analyses:—

	I. Per cent.	II. Per cent.
Carbon . . . . .	1·70	3·40
Silicon . . . . .	2·40	0·85
Sulphur . . . . .	0·55	1·50
Iron . . . . .	23·30	32·35
Nickel . . . . .	75·50	60·90

From these it is seen that in spite of the addition of limestone the alloy still contained an appreciable amount of sulphur. The ferro-nickel was exported to Europe, where it was attempted to purify it from sulphur, silicon and iron by oxidising processes. For example, at Septèmes, near Marseilles, the alloy was fused on a hearth of nickel monoxide in a Siemens-Martin furnace, and finally a crude nickel containing manganese was added to remove the oxygen. A lining of chalk to the hearth was also used to remove the silicon and sulphur.

This operation attained its aim just as little as any of the other diverse methods that have been tried, inasmuch as it was not successful in removing iron and sulphur from the nickel. Consequently the production of the nickel-iron alloy has been entirely given up.

At present all the ore raised in New Caledonia is exported. The greater part comes to Europe, and there is smelted into a matte in blast furnaces with the addition of materials containing sulphur. This matte is refined in reverberatory furnaces or converters, or by roasting and smelting in shaft furnaces, and lastly worked up by roasting into nickel oxide, or into nickel by roasting and afterwards reducing. These processes are carried on chiefly in Glasgow, Birmingham, Havre, and at the works of the French "Le Nickel" Co. at Iserlohn.

The ores are smelted in shaft furnaces, which are surrounded with water jackets either throughout their height, or from the bottom to 3 feet 3 inches high. Coke and fluxes containing sulphur are added and the product is a coarse matte. The flux chiefly used is the calcium sulphide, remaining in the manufacture of soda by the Leblanc process; if this cannot be obtained, gypsum is used. By the use of this flux, the whole of the nickel and part of the iron pass into

matte. The calcium sulphide is decomposed by the nickel silicate of the garnierite, and nickel sulphide and calcium silicate are formed. If gypsum is used it becomes reduced to sulphide in the furnace by the coke, and the action with garnierite then proceeds. The ore is crushed to powder with gypsum and coal, and this mixture pressed into bricks. In 24 hours 25 to 30 tons of ore are put through one of these furnaces. Levat gives the consumption of coke as 30 per cent. of the ore. The matte contains 50—55 per cent. Ni, 25—30 per cent. Fe, and 16—18 per cent. S, and is free from arsenic and copper. Just as above with nickel coarse matte, this can be freed from iron and an equivalent quantity of sulphur in reverberatory furnaces or converters. A refined matte is then obtained with an average composition of 75 per cent. Ni, 24 per cent. S, 0.5 per cent. Fe, and 0.5 per cent. of various impurities. Just like the refined matte from the other ores, this is dead roasted, and reduced to nickel.

The slag obtained from the ore smelting is thrown away. If the matte is to be refined by roasting, and then fusing with sand, this operation is performed in the same furnaces with water jackets as are used for the ore. The slag obtained in the refinery contains large quantities of nickel; it is made into bricks after being ground with sand, gypsum and coal, and smelted to a matte in the same furnaces. This matte is subjected to a smelting to concentrate it, and then treated in the same way as the coarse matte obtained from the ore.

Near Frankenstein in Silesia,<sup>1</sup> nickel silicate occurs as schuchhardtite (4 to 23 per cent. of nickel), pimelite (5 to 7 per cent. of nickel) and garnierite (15 to 18 per cent. of nickel), and in lenticular patches in serpentine at Gläsendorf, Kosemitz, Zülzendorf, Baumgarten and Grochau. The ores at present produced in the Martha and Benno mines at Gläsendorf and Kosemitz, are treated at the Martha works near the mine of that name. Their average composition is:—

SiO <sub>2</sub> . . . . .	60	to 65.4	per cent.
MgO . . . . .	8.5	„ 12	„
Fe <sub>2</sub> O <sub>3</sub> } . . . . .	6	„ 8	„
Al <sub>2</sub> O <sub>3</sub> }			
Ni . . . . .	2.3	„ 3.5	„
Loss on ignition } . . .	8	„ 15	„
(chiefly water) }			

<sup>1</sup> Illner, *Zeitschr. für Berg-, Hütten- u. Salinenwesen im Preuss. Staate*, 1902, p. 816.

The ores are almost free from copper, for at most they contain 0.0032 per cent. They are first smelted with bodies containing sulphur in shaft furnaces, yielding thereby crude nickel matte. This is roasted in reverberatory furnaces and then concentrated in shaft furnaces, and the concentrated matte is refined in converters. The refined matte is roasted sweet and then reduced to nickel.

Gypsum or anhydrite is used as the sulphurous addition, and limestone or sludge from the sugar works as slagging material. The charge is made of 100 parts of ore, 10 of gypsum or 7 of anhydrite, 22 of limestone or 30 to 33 of sludge. It is crushed in stone breakers and rolls to half-inch fragments and pressed into bricks without binding material; the bricks are dried and smelted with coke for crude matte. The smelting takes place in shaft furnaces 16 feet 4 inches high and 19 square feet in cross-sectional area at the tuyeres; 50 parts of coke are used for 180 parts of ore. Each of the two furnaces used at the Martha works puts through 25 tons of ore in 24 hours, and produces from 100 tons of ore 7 tons of crude matte, containing:—

Ni . . . . .	31.40 per cent.
Fe . . . . .	49.71 „
S . . . . .	14.50 „

The slags from this operation are very pasty; they contain 62 to 71 per cent. of silicon and 0.3 per cent. of nickel, and are used to make slag bricks.

The crude matte is crushed in rock-breakers and ball mills and roasted in long-bedded reverberatories having 2 hearths, one above the other, each 20 feet long and 7 feet wide. In 8 hours 6 cwts. of matte are roasted, and the roasted matte contains:—

Ni . . . . .	15 to 25 per cent.
Fe . . . . .	33 „ 45 „
S . . . . .	3 „ 8 „

This is smelted in a cupola furnace 7 feet 4 inches high and 2 feet 8 inches in diameter, with coke and sandstone, and it yields a concentrated matte containing:—

Ni . . . . .	65 per cent.
Fe . . . . .	15 „
S . . . . .	20 „

The slags from this operation contain 2 to 3 per cent. of nickel, 52 per cent. of iron and 42 per cent. of silicon. They are added to ore-smelting charges.

The concentrated matte is transferred to a converter and blown for refined matte. The converter holds 6 cwts. of matte; sand is added during the blow, which lasts for 45 minutes. The refined matte is cast in moulds and treated for nickel. It has the composition:—

Ni . . . . .	77·84 per cent.
Fe . . . . .	0·26 „
S . . . . .	21·31 „
Cu . . . . .	0·19 „ (maximum).

The slag contains up to 10 per cent. of nickel and is added in the smelting of the roasted matte. This refined matte is crushed in rock-breakers and ball mills, and the sulphur removed down to 1 per cent. by roasting in long-bedded reverberatories. The roasted mass is again crushed and completely roasted in a reverberatory furnace to nickel oxide; this contains 77·65 per cent. of nickel, 0·10 of iron and 0·0088 of sulphur.

The nickel oxide is ground between mill-stones to a fine powder, mixed to a paste with 0·5 per cent. of meal, moulded into cubes of  $\frac{1}{2}$  inch side or into cakes, then dried and reduced to metallic nickel with addition of 25 per cent. of charcoal. This is performed in vertical tubes 30 inches high and 8 inches in diameter, which are closed on top with a fire-clay lid. The tubes stand in 2 rows of 10 each in a furnace fired by gas, with regenerators, the length of the furnace being 13 feet 4 inches, its breadth 6 feet 8 inches. The reduction is complete after 3 hours. The tubes are discharged through the bottoms, which are closed with sliding fire-clay tiles. The nickel is obtained in the form of cubes or cakes, and contains:—

Ni . . . . .	99 per cent.
Fe . . . . .	0·3 „
Cu . . . . .	0·2 „
Insoluble residue . . . . .	0·5 „

The yield of nickel from the ores is stated to be 1·9 per cent. Sulphur dioxide and trioxide generated during the roasting are absorbed by lime, and the mixed sulphite and sulphate of calcium thus produced is converted entirely into sulphate by standing in air. This sulphate is then used in smelting the ores.

### 3. EXTRACTION OF NICKEL FROM ARSENICAL ORES

The arsenical ores are niccolite or kupfernickel, chloanthite and nickel glance. Only a very small amount of nickel is obtained from these ores, owing to their limited occurrence. Besides gangue, these nickel ores generally contain large quantities of iron, and often

sulphur. The metallurgical processes consist in getting rid of the gangue, and separating nickel from iron, arsenic and sulphur. The separation of nickel from iron depends on the fact that the chemical attraction of iron for oxygen is greater than that of nickel, whilst the affinity of arsenic for nickel is greater than its affinity for iron. It is therefore possible to oxidise and slag the iron in the ore, while the nickel is separated as arsenide.

At a sufficiently high temperature nickel arsenide is converted by the oxygen of the air into a mixture of nickel monoxide and arseniate. The latter is mostly converted into monoxide by strongly heating with carbon, and afterwards in a current of air. Another way is to remove the arsenic of nickel arsenide as an alkaline arseniate by heating with saltpetre and soda, while the nickel is converted into monoxide. Washing with water removes the alkaline arseniate from this oxide. The nickel monoxide is reduced to nickel as described above.

The production of pure nickel arsenide or nickel speiss from the ores entails roasting and smelting operations. If the ores contain sulphur, or more arsenic than is required to form the compound  $\text{Ni}_2\text{As}$ , they are subjected to an oxidation to remove the sulphur and excess of arsenic; and then reduced in shaft furnaces. But if the ores contain no metallic sulphides and no excess of arsenic but only gangue, they are subjected at once to a smelting, with formation of slag, in shaft furnaces.

Since as a rule there is a large proportion of arsenide of iron in the ores, a speiss is generally obtained which contains iron, which is known as "coarse" speiss; and it rarely consists of only nickel arsenide. It is roasted in order to oxidise it, after which it is smelted in reverberatory or shaft furnaces; it may also be fused and oxidised on a hearth or in a reverberatory furnace, which removes the iron and a corresponding amount of the arsenic. If the speiss is poor in nickel and rich in arsenic and iron, these operations will have to be repeated. The nickel speiss free from iron, which is finally obtained—"refined nickel speiss"—is completely roasted in reverberatory furnaces, carbonaceous bodies being mixed with it from time to time to help to remove the arsenic, and at the end of the process saltpetre and soda are added. In this way nickel monoxide is formed, and is reduced in the usual manner.

We must thus distinguish three operations:—

- a. Conversion of ore into coarse speiss.
- b. Conversion of coarse speiss into refined nickel speiss.
- c. Conversion of refined nickel speiss into nickel.



### a. CONVERSION OF ORE INTO COARSE SPEISS

The basis of this conversion is the following: Ores which contain sulphur, arsenide of iron, or more arsenic than is required to form the compound  $\text{Ni}_2\text{As}$  are calcined and then reduced in shaft furnaces; ores free from sulphur or arsenide of iron, and not containing excess of arsenic, are smelted direct in reverberatory or shaft furnaces with the object of producing a slag.

#### *a. Roasting the Ores*

When the ores are free from sulphur, the roasting should be regulated so that the arsenic is brought down to the quantity sufficient to combine with the whole of the nickel to form  $\text{Ni}_2\text{As}$  as the main product of the subsequent smelting. If the roasting is carried too far, and the quantity of arsenic is less than this, nickel will pass into the slag. When sulphur is present, the roasting should remove it as completely as possible, unless there is also copper enough to be worth extracting. In this case sulphur should be retained in such quantity that a copper matte is formed during smelting, and separates from the speiss.

During the roasting arsenic is converted partly into arsenic trioxide, partly into pentoxide. The iron and the nickel arsenides lose arsenic and become converted into oxides. The higher compound of arsenic is formed by the oxidation of the trioxide where it is in contact with red-hot masses of ore, and the red-hot furnace walls; it combines partly with the iron and nickel oxides (with cobalt oxide and with silver also if present). Further, part of this arsenic pentoxide is reduced again to trioxide by contact with undecomposed arsenides, and with the lower metallic oxides, if any should be present. Arseniate of nickel is much more easily produced than the corresponding salt of iron. The arseniates are fairly stable at a high temperature, as they are not readily decomposable by heat alone. If it is desired to remove the arsenic from them, powdered coal or carbonaceous matter is added. By these means iron arseniate is somewhat readily converted into ferric oxide, while the acid radicle is converted into arsenic trioxide and suboxide, with the formation of carbon dioxide. Arseniates of cobalt and nickel are converted into arsenides, which, in a current of air, are converted into oxides and basic arseniates, with a loss of some arsenic as trioxide. The product of the roasting is accordingly a mixture of undecomposed arsenides, oxides and basic arseniates.

If metallic sulphides are present in the ores they are oxidised to sulphates. Vapours of sulphur trioxide are formed from sulphur dioxide by contact action, or from the decomposition of sulphates, and exert an oxidising action on arsenides, which are partly converted into arseniates. Any arsenical pyrites (iron sulphate and arsenide) present in the ore, gives off fumes of sulphide of arsenic; at a red heat it is converted into a mixture of ferric oxide, sulphate and arseniate, setting free sulphur dioxide and arsenic trioxide.

Carbonates of iron and calcium, which are frequently present in nickel ores, are changed into arseniates of those metals, or into a mixture of sulphates and arseniates if sulphides are present. During this heating the heat must not be carried so high that any silica present forms silicate with nickel monoxide, because this nickel silicate is but imperfectly decomposed again, in the subsequent smelting, with the formation of arsenide of nickel. Thus, if sulphides are present in the ore, the product of roasting is a mixture of metallic sulphides, arsenides, oxides, sulphates and arseniates.

The roasting may be performed in heaps, stalls, reverberatory or shaft furnaces, or muffles. Since the complete removal of the arsenic is not really necessary, the ores are roasted in stalls in most works, these stalls allowing of the collection of arsenic trioxide in the chambers attached.

The best forms of apparatus for roasting are reverberatory furnaces and muffles. In the latter it is very easy to attain exactly the desired limit in roasting. If it is necessary to make the fumes quite harmless, or to collect the whole of the arsenic trioxide formed, they should be used.

Stalls were or are in use at Schladming in Styria, Dobschau in Hungary, and Leogang in Salzburg.

At Schladming,<sup>1</sup> ores containing 11 per cent. of nickel and 1 per cent. of cobalt were roasted in so-called Bohemian roasting stalls: 16½ feet long, 15 feet wide and 4 feet high, which were connected with condensing chambers for sulphide of arsenic and arsenic trioxide. On the brick bottom of the stall was spread 5 inches of wood and a quarter of an inch of wood charcoal; on this 18 or 20 tons of ore spread out to a thickness of about an inch. In the long axes of the stall were two square wooden conduits, to improve the draught, and these were in connection with canals in the floor left free from ore. Before firing the stall a layer of fine ore was placed on the surface of the charge, and then the stall bricked up. Firing was done

<sup>1</sup> Badoureaux, *Berg- und Hütt. Ztg.*, 1878, p. 205.

<sup>2</sup> *Allg. Hüttenkunde*, p. 328.

by shovelling red-hot coals in at the wooden conduits. The roasting lasted 5 to 8 days.

At the George Smelting Works at Dobschau in Hungary, ore containing 4·5 per cent. of nickel and 1·5 per cent. of cobalt was roasted in stalls with arched roofs 10 feet high,  $16\frac{1}{2}$  feet long, and 13 feet wide, connected with condensing chambers; 40 tons of ore formed the charge in one stall. The bed was formed of  $1\frac{3}{4}$ –2 cords wood. The roasting lasted 2 to 3 days.

At the Losonez Works in Hungary,<sup>1</sup> ores containing 14 to 20 per cent. of nickel with cobalt and 0·5 per cent. of copper were roasted

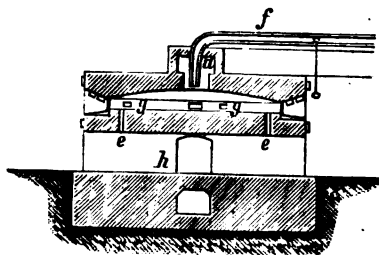


FIG. 468.

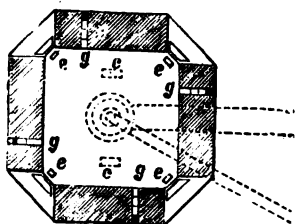


FIG. 469.

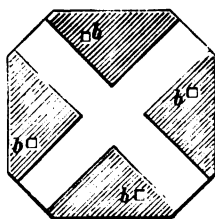


FIG. 470.

in reverberatory furnaces on beds 10 feet square in charges of 16 cwt. to 1 ton. Wood was used as fuel.

A reverberatory gas-furnace designed by Flechner<sup>2</sup> for the roasting of ores and speiss is depicted in Figs. 468–470. It is said to be used at Schladming, and (with direct firing) in Westphalia. The gas enters the middle of the furnace through the channel *a*, and the air necessary for its combustion is led in through the pipe *f*.

The products of combustion pass through four openings (up-takes) *g*, built in the side walls of the furnace, into the perpendicular channels *b*, and thence into the chimney. The ore is charged into the furnace through two openings *c* in the roof. The working

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 206.

<sup>2</sup> *Ibid.*, 1879, p. 211.

openings are at the four corners of the furnace. In front of each of these is a perpendicular shaft *e*, which is connected with the intersecting passages *h*. Waggon's are wheeled into the latter in order to remove the roasted products when emptied through the channels *e*.

### *β. The Smelting of the Nickel Ore into Coarse Speiss*

If gangue only has to be separated from the nickel arsenide, the ores are smelted in blast or reverberatory furnaces with the addition of fluxes and slag-forming materials. The slagging away of the gangue is the only chemical change aimed at in this process.

But if the ores have been roasted beforehand, and now consist of mixed oxides, arseniates and undecomposed arsenides, with often sulphates and sulphides as well, then the whole amount of nickel in the roasted product has to be collected into a speiss, the gangue to be completely slagged, and the iron as far as is possible. Any copper worth extracting should be collected in a matte. This sort of smelting is usually performed in a blast-furnace, but can also be carried out in a reverberatory furnace.

In the blast furnace used as a rule on the Continent, ferric oxide is reduced to ferrous and slagged with silica. Nickel monoxide is partly reduced to metal, partly reacts with iron arsenide to form nickel arsenide and ferrous oxide, which latter is also slagged by silica. The metallic nickel takes arsenic from compounds of nickel containing it in larger proportion, and  $\text{Ni}_2\text{As}$  is thus formed, or it takes arsenic from iron arsenide. This latter is thereby reduced to a compound containing less arsenic, or iron is separated if such compounds cannot be formed. The iron may be taken up by the speiss, but part of it reacts with ferric oxide to form ferrous oxide which is slagged.

Nickel arseniate is reduced to arsenide. Iron arseniate loses most of its arsenic in the upper part of the furnace, and arsenic pentoxide is reduced to trioxide by the action of carbon monoxide; this trioxide volatilises, while carbon dioxide is also formed, and ferric oxide is left, which is reduced to ferrous oxide and slagged.

If metallic sulphides, and sulphates of copper and iron are present, the same changes occur as stated above in the smelting of roasted nickel ores containing sulphur. Copper sulphide unites with any metallic sulphides that remain to form a matte. Nickel arsenide unites with any remaining iron arsenide, or other arsenides that may be present, to form a speiss. If the copper present finds no sulphur to combine with, it passes into the speiss. If the matte is in very



small quantities it is taken up by both slag and speiss, otherwise it separates out above the speiss.

Earthy matter present, as well as most of the iron, passes into the slag. If there is not enough arsenic present to combine with all the nickel, a corresponding portion is slagged off. Any nickel silicate present, formed by too great heat in the roasting, goes for the most part into the slag. Nickel silicate and iron arsenide do not readily interact, so it is not possible to get back all the slagged nickel into the speiss by such a change.

The smelting is conducted so that a monosilicate containing at least 30 per cent. of ferrous oxide is formed. An acid slag will contain nickel. (According to Badoureaux, when nickel and cobalt arsenide are smelted together with a slag containing 30 per cent. of ferrous oxide, the two former metals are practically not slagged at all.) Otherwise the same principles are observed in the formation of the slag as were laid down above for its formation in smelting the sulphuretted nickel ores in blast furnaces. Further, with regard to the arrangement of the furnaces and conducting of the operation, all that has been said there still applies. The furnaces are constructed usually as crucible furnaces or have fixed fore-hearths.

Kupfernicks containing heavy spar used to be smelted at Sangerhausen<sup>1</sup> without previous roasting. The blast furnace, constructed as a crucible furnace, was  $6\frac{1}{2}$  feet high and 1 foot wide. 1 lb. fluorspar was added as flux to 100 lbs. ore, together with 2 lbs. clay and 4 lbs. quartz, and also a measured quantity of slag from a previous operation. 100 lbs. of ore required  $15\frac{1}{2}$  cb. ft. charcoal. The speiss obtained contained about 40 per cent. of nickel. As instances of the smelting of roasted ore, we may take Schlading in Styria, Dobschau in Hungary, and Leogang in Salzburg.

At Schlading,<sup>2</sup> where the ore was roasted in stalls, and contained 11 per cent. of nickel and 1 per cent. of cobalt, it was smelted in blast furnaces with crucible hearths,  $6\frac{1}{2}$  feet high, provided with one tuyere in the back wall. This furnace had a trapezoidal horizontal section,  $1\frac{1}{2}$  feet wide in the tuyere wall, 1 foot 9 inches wide in the front wall, and 2 feet deep. The tuyere was 5 feet 7 inches below the mouth, and 10 inches above the bottom. The crucible had two tap holes, each of which communicated with a fire-hearth. These hearths were made of slag from ore smelting, worked into a paste with milk of lime. The charge consisted of 89 parts roasted ore, and 19 parts quartz. In 24 hours 5 tons of ore were put through, with the use

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1864, p. 59.

<sup>2</sup> *Ibid.*, 1878, p. 205.

of 18 cwt. of charcoal. The speiss, which was tapped every two hours, contained :—

45 to	47	per cent.	Ni
4	„	6	„ „ Co
8	„	10	„ „ Fe
1	„	1.5	„ „ Cu
33	„	36	„ „ As
1	„	2	„ „ S
1	„	2	„ „ Charcoal

At the George Works at Dobschau<sup>1</sup> in 1876, the ore contained 4.5 per cent. of nickel and 1.5 per cent. of cobalt, and was roasted in stalls. It was then smelted in blast furnaces 16½ feet high, circular in horizontal section, and having two tuyères. The diameter was 3 feet 4 inches at the level of the tuyere, 4 feet at the mouth. The tuyere was 2½ inches in diameter, the blast pressure 2½ inches of mercury. The charge was 100 parts ore, 3–4 quartz, 8–12 limestone, 5–10 rich slag. In 24 hours 7 to 10 tons of ore were put through, with one-fifth the amount of charcoal. The speiss obtained contained from 16 to 20 parts per cent. of nickel and cobalt.

At Leogang in Salzburg,<sup>2</sup> the calcareous ore containing 2 to 3 per cent. of nickel and cobalt was roasted in stalls, and smelted with the addition of quartz in blast furnaces 4 feet high and 2½ × 2½ feet in plan. The slag obtained contained some cobalt.

The smelting of the ore in reverberatory furnaces is said to be practised only in England. In such the nickel monoxide and arseniate formed in the roasting react with iron arsenide to form ferrous oxide and nickel arsenide. The iron is slagged. Instances of this method have not come to the knowledge of the writer.

#### b. CONVERSION OF COARSE SPEISS INTO REFINED NICKEL SPEISS.

This conversion, which aims at the removal of the iron with its equivalent of arsenic, consists either (1) in roasting the coarse speiss and then smelting it in blast furnaces, and, if necessary, repeating the whole process on the speiss obtained; or else (2) roasting, smelting in reverberatories, and always repeating the operation on the insufficiently pure product; or else (3) smelting the roasted coarse speiss in crucibles; or else (4) taking the speiss formed by roasting the coarse one and smelting in either of the two sorts of

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, p. 206.

<sup>2</sup> *Ibid.*, p. 206.

furnaces, then subjecting the product to an oxidising fusion in a reverberatory furnace without previous roasting.

The chemical changes in roasting the speiss are the same as in roasting the ore.

The changes in smelting this roasted speiss in blast furnaces are the same as for similar smelting of roasted ore, except for the slagging of the earthy matter. When the smelting takes place in a reverberatory furnace, the changes are chiefly these: iron arsenide reacts with nickel monoxide and arseniate to form ferrous oxide and nickel arsenide. The ferrous oxide is slagged by means of the silica present in the hearth, or added, or by the addition of potash and soda, while nickel forms a speiss.

Smelting in crucibles entails the same changes as smelting in reverberatory furnaces.

When unroasted speiss undergoes an oxidising fusion in hearths or reverberatories, the iron is first oxidised or converted into iron arseniate (as in the Plattner nickel assay), and then is slagged by means of sand, glass and quartz strewed on the molten metal. After iron follows cobalt, and nickel after that. The process of oxidation can be so regulated by repeated drawing off of slag, and repeated strewing of sand or poor quartzose ores on the molten mass, that nickel remains combined as arsenide, while iron passes into the slag.

The roasting of the speiss is carried on in stalls or reverberatory furnaces. Here also condensing chambers are added to make the products harmless, or to collect the arsenic trioxide. The Flechner reverberatory furnace described above <sup>1</sup> has been used, with specially good results, either with gas or with direct firing.

The blast furnaces for smelting are similar to those used for ore.

Among reverberatory furnaces for smelting the speiss or for refining it by a blast, the Hungarian furnace and the Flechner one with gas deserve mention.

The arrangement of the Hungarian reverberatory furnace <sup>2</sup> is shown in Figs. 471, 472.

The bed *S* of the furnace, which is 8 feet long and 6½ feet in maximum width, consists of layers one above the other of slag, clay, sand and marl. The smelting hearth is hollowed out in the marl layer. *C* is the roof over the hearth-bed, 2 feet 7 inches high; at the highest point *f* are openings, for the admission of air, 2½ inches

<sup>1</sup> P. 703.

<sup>2</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 206; Kerl, *Metallhüttenkunde*, p. 538.

wide at the nose. Through these, air at a pressure of  $10\frac{1}{2}$  inches of water is blown into the hearth-chamber. The fire-grate is 4 feet 2 inches long and  $2\frac{1}{2}$  feet wide. This contains two grates, *R* and *r*,

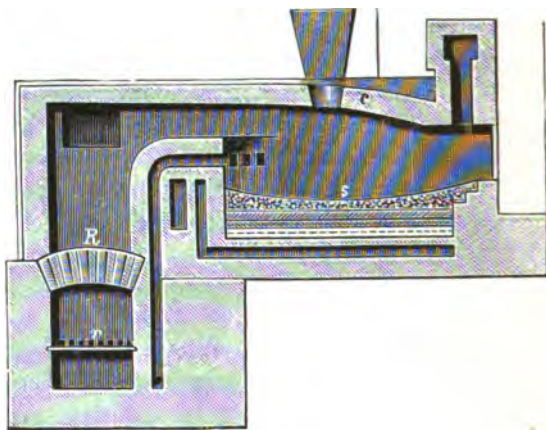


FIG. 471.

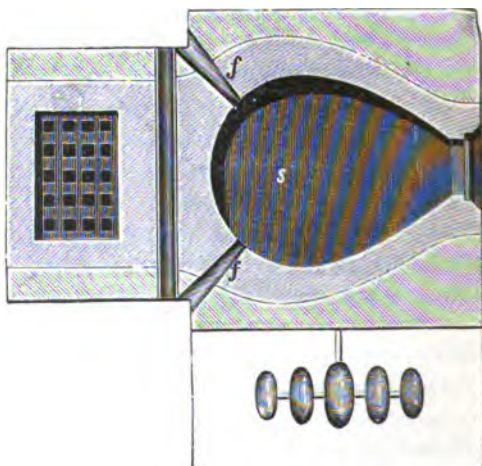


FIG. 472.

one over the other, of which the upper *R* is made of slag bricks, the lower *r* of iron bars. Wood is burnt on the upper grate; the charred sticks fall through the interstices, shown in the figure, on to the iron grate underneath, where they are completely burnt.

The construction of Flechner's reverberatory furnace with gas fuel is shown in Figs. 473 to 478.



*A* is the gas-producer, *B* the hearth, *C* the flue. The air for the combustion of the gases enters at *D*, and ascends through the

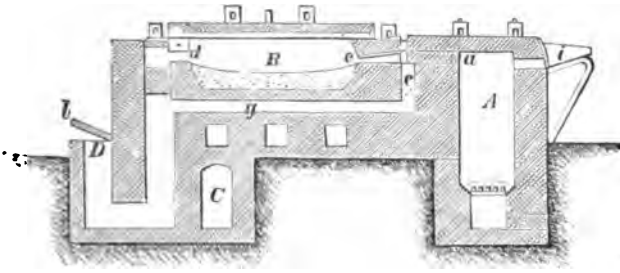


FIG. 473.

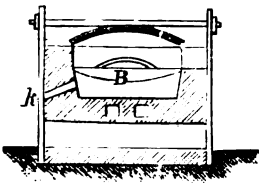


FIG. 474.

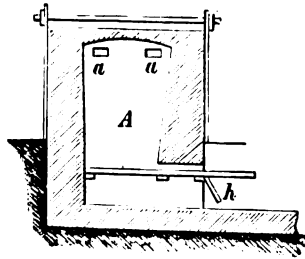


FIG. 475.

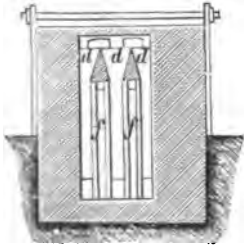


FIG. 476.

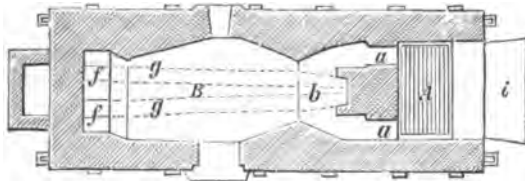


FIG. 477.

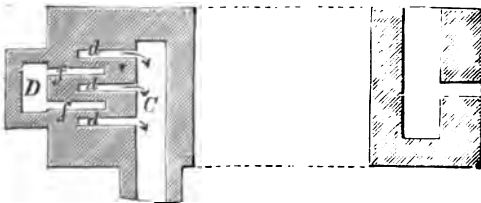


FIG. 478.

channels *f*, which are placed between *d*, *d*, the exit-flues for combustion products. It is warmed in the pipe *g*, passing under the hearth of the furnace, and then passes on through the ports *c* into

the chamber *b*, where it is mixed with the gases streaming out from the producer through the channel *a*. The burning gases pass through the port *e* into the heating chamber, and thence through the port *d* into the chimney *C*. Through the hopper *i* the fuel is introduced into the producer. The roof of the furnace is movable on hinges. The air for combustion is regulated by the valve *l*.

At the George Works at Dobschau,<sup>1</sup> coarse speiss containing 16 to 26 per cent. of nickel and cobalt was roasted in stalls with from 3 to 5 firings, and then smelted to a concentrated speiss in blast furnaces similar to those used for the ore.<sup>2</sup> In 24 hours 11 tons of speiss, with 23 per cent. of quartz and 26·5 per cent. of charcoal, were put through. The concentrated speiss contained—

Ni and Co . . . . .	31·9 per cent.
Cu . . . . .	1·9 „
Fe . . . . .	26·4 „
As . . . . .	36·3 „
S . . . . .	3·1 „

This speiss was roasted three or four times in stalls, and then again smelted to a doubly concentrated speiss in one of the Hungarian furnaces described above. The charge in it was 1·8 to 2 tons of roasted speiss. When the roasted material was all fused, which took 10 hours, the air blast was turned on, and glass, quartz and soda were added. To prevent cobalt in appreciable quantity from being slagged, the whole of the iron was not removed, but the blast stopped when the iron, all but 8 or 10 per cent., was removed (after 12 to 14 hours). 100 parts of the roasted concentrated speiss required 2 parts of glass, 4 of quartz and 1 of soda. The doubly concentrated speiss had this composition:—

Ni and Co . . . . .	50—52 per cent
Cu . . . . .	1—2 „
Fe . . . . .	8—10 „
As . . . . .	38—40 „
S . . . . .	1—2 „

The slag contained 1 or 2 per cent. Ni and Co, and was added to ores during smelting. From the doubly concentrated speiss nickel and cobalt were extracted.

At the Maudling Works<sup>3</sup> in Austria, the coarse speiss from

<sup>1</sup> *Berg-und Hüttenm. Ztg.*, 1878, p. 206.

<sup>2</sup> P. 706.

<sup>3</sup> *Berg-und Hüttenm. Ztg.*, 1878, p. 206.

Schladming in Styria was worked up. It contained 45 to 47 per cent. of nickel and 4 to 6 per cent. of cobalt. It was first roasted in a reverberatory furnace with octagonal hearth and 8 working doors, the central fireplace being situated under the middle of the bed. After this it was smelted in graphite crucibles with potash and quartz. The crucibles were placed 8 in each air furnace, and each contained 35 to 45 lbs. of the roasted coarse speiss, with 30 per cent. potash and 12 per cent. quartz. The heating of this furnace took 3 hours, then the fusion took place after 6 hours more; the crucibles remained 17 more hours in the fire, and then were taken out and emptied. In 24 hours 194 cub. ft. charcoal were used. 100 parts of roasted coarse speiss gave 55 refined speiss with 67 per cent. of Ni, Co and Cu, 2 per cent. of Fe and 31 per cent. of As. The slag was a mixture of arseniates and silicates of cobalt and iron.

At Leogang in Salzburg,<sup>1</sup> the coarse speiss was roasted in stalls three or four times, and then smelted to a concentrated speiss in blast furnaces with quartz and slag from the first smelting. The latter speiss was subjected to a blast in a Hungarian reverberatory furnace on a quartz bed. The blast was continued with repeated removal of slag and addition of sand until all the iron was slagged. The slag resulting contained cobalt, and was smelted with quartz and arsenic into a cobalt speiss.

### c. CONVERSION OF REFINED SPEISS INTO RAW NICKEL

This conversion is effected by a complete roasting of the speiss and subsequent reduction to metal.

#### a. *The Dead Roasting of Refined Nickel Speiss*

The object of this is to convert the arsenide of nickel entirely into monoxide. It is done by repeated roasting, the decomposition of any arseniate formed being ensured by the addition of carbonaceous matter, or part of the arsenic may be converted into alkaline arseniate by the addition of saltpetre and soda during the roasting. Again, the two treatments may be combined, and first carbonaceous matter, secondly saltpetre (alone or with soda) added to the speiss during roasting.

Nickel arsenide is oxidised to monoxide and to arseniate, while arsenic trioxide escapes. The arseniate may be made to give off

<sup>1</sup> *Berg-und Hüttenm. Ztg.*, 1878, p. 206.

some arsenic and form a basic compound by raising the temperature. But in presence of carbon it is reduced to arsenide, which again becomes converted partly into monoxide, partly into arseniate, by oxidation, while more arsenic trioxide is given off. The amount of arseniate present thus diminishes, and in this way, by alternate oxidation, and reduction, all the arsenic is finally removed.

Again, the addition of saltpetre to the charge converts the arsenic into an alkaline arseniate, easily removed by washing with water. By taking advantage of this action the last portions of arsenic and



FIG. 479.

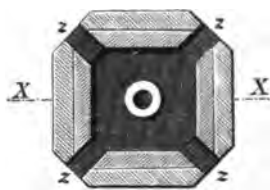


FIG. 480.



FIG. 481.

of sulphur are removed, the sulphur as alkali sulphate. Frequently soda, or soda and salt, is added with the saltpetre. By the action of the salt some arsenic chloride (and antimony chloride from any antimony present) are formed and volatilised.

(Apart from roasting, arsenic may be removed also by smelting the speiss with saltpetre and soda, or smelting it with soda and sulphur, and washing out the salts formed; or it can be removed in the form of sulphide of arsenic by heating the speiss with sulphur in absence of air.)

At Schladming<sup>1</sup> the refined speiss was completely roasted in a furnace, of which the construction may be seen in Figs. 479 to 481.<sup>2</sup>

The fireplace *f* lay under the hearth *H*, which was 6 feet 6 inches square. The gaseous products of combustion passed up the perpendicular chimney *k* opening into the heating chamber in the middle of the hearth. They left this latter by four openings *z* at the four corners, which openings served also as working ports, then into chimney hoods over the corners, and over the arch of the furnace into the chimney *y*.

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 228.

<sup>2</sup> *Kerl, Metallhüttenkunde*, p. 548.

The charge in the furnace was 4 cwt. of speiss, which was dead roasted in 24 hours, using wood fuel. After 20 hours had elapsed, about 45 lbs. of a mixture of equal quantities of saltpetre and soda was added, which converted the arsenic still present into alkaline arseniate. This was dissolved out after the roasting, in a tub with water. The residue consisted of nickel oxide.

At the George Works at Dobschau in Hungary, the refined speiss was roasted, in 1867, in a reverberatory with double hearth. Towards the end of the first roasting, pine needles or charcoal dust was added to the mass at intervals of about half an hour. The product was sieved and ground, and then mixed with 10 per cent. of its weight of soda, 5 per cent. of saltpetre, and 10 per cent. of sea salt, and subjected to a second roasting for 4 hours. In this, arsenic and antimony were partly volatilised as chlorides, partly converted into alkaline arseniates and antimonates. On account of these the mass remained pasty for 2 hours. After the roasting the arseniates and antimonates were removed by repeated washing with hot water.

### *β. Reduction of Dead Roasted Speiss to Crude Nickel*

This is done in the same way as the reduction of a completely roasted matte of nickel, given above. If the speiss contains copper, so will



FIG. 482.

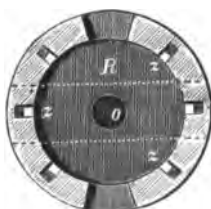


FIG. 483.

the crude nickel. At Schladming in Styria, from 1860 to 1867,<sup>1</sup> the dead roasted and ground speiss was mixed with 4 per cent. of syrup, and made up on a tin plate into cakes weighing 3.7 lbs., 6 inches wide, 10 inches long, and  $\frac{1}{8}$  inch thick; these were dried and cut into cubes. The cubes were dried in the sun or in a baking-oven and reduced to metal in crucibles of fire-clay. Each crucible took a charge of 26 to 29 lbs. of the cubes of nickel monoxide, with 3 lbs. of

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 244.

coal dust; 40 crucibles were placed in a round furnace, represented in Figs. 482, 483. *R* is the heating chamber which receives the crucibles; the fireplace is below it. The products of combustion pass from the fireplace *r* through an opening *o* in the middle of the bed, into the heating chamber, thence through 6 flues *z* into a chamber above the arch of the furnace, thence into the chimney *v*.

The heating of the crucibles, performed with wood fuel, lasted 48 hours. At each operation 7 cwt. of crude nickel were obtained.

## B. EXTRACTION OF NICKEL FROM METALLURGICAL PRODUCTS

Nickel or its alloys can be extracted in the dry way from various metallurgical residues, particularly from certain forms of speiss obtained from copper, lead and silver ores which contain nickel as an impurity, often very slight in quantity. Further, coarse or blister-copper frequently contains nickel, which collects in this product if there is but little arsenic in the copper ore; and there are also slags and iron sows containing nickel.

The speiss is worked up in the same way as the coarse speiss obtained in the extraction of nickel from its arsenical ores. If it contains large quantities of lead, copper and silver, it is sought to separate lead and silver as an alloy (argentiferous lead) and the copper as a matte. Lead may always be removed from the speiss by roasting and reduction, and takes with it the greater part of any silver that may be present. Thus most of the silver is disposed of in the same process. The copper is converted into sulphide by smelting with heavy spar, or with pyrites if that cannot be obtained. There results after these operations a speiss richer in nickel and mostly free from the other metals, and this is worked up by the processes mentioned above.

So, for example, at Freiberg, a speiss containing all three of the above metals served for the extraction of the three, and was smelted several times in a blast furnace with the addition of heavy spar, lead residues and slag, and was converted into argentiferous lead, copper matte, and a speiss containing but little silver, lead or copper. The speiss thus enriched in cobalt and nickel up to 15 or 18 per cent. was smelted in a reverberatory furnace without any previous roasting, with the addition of 50 to 60 per cent. of heavy spar and 20 to 25 per cent. of quartz; the products were, a copper matte containing lead, and a speiss containing 40 to 44 per cent. of nickel, 8 per cent. of copper, and free from iron.

Copper containing nickel is subjected to a blast, which gives a dross containing nickel, and copper free from it. The dross may be smelted in a blast furnace again to coarse copper containing nickel, or it may be smelted into a speiss when large quantities of arsenic and antimony are present. This coarse copper from the dross, called dross or waste copper, gives on refining or subjecting to the blast a second dross richer in nickel and cobalt. By smelting this in a furnace, copper still richer in nickel is obtained. So by the repetition of the processes the final result is a nickel-copper alloy, which is sold to the nickel works.

Or again, the dross may be smelted with pyrites to a matte containing nickel, or with heavy spar and arsenical pyrites to a speiss and a copper matte. Again, nickel can be extracted from coarse copper in the wet way.

The metal is obtained from slags containing nickel without copper by smelting them in blast furnaces with heavy spar or pyrites, yielding a nickel-bearing matte, or with arsenical pyrites, giving a nickel speiss. But if the slag holds copper in quantities worth recovering, the smelting is carried on with arsenical pyrites and either heavy spar or iron pyrites, so as to obtain nickel in a speiss, copper for the most part in a matte. This does not effect a satisfactory separation. It is therefore necessary, in case the separation is very incomplete, to treat again the speiss containing copper and the matte containing nickel with heavy spar and arsenical pyrites.

For example, in Altenau the slags from the refining of dross copper, containing both copper and nickel, were smelted in blast furnaces with iron pyrites and arsenical pyrites to a speiss and a matte of the following compositions :—

	Speiss.		Matte.
Ni and Co . . . . .	26·77	. . .	6·10
Cu . . . . .	19·85	. . .	37·24
Fe . . . . .	15·82	. . .	20·84
Pb . . . . .	12·14	. . .	16·10
As . . . . .	12·15	. . .	trace
Sb . . . . .	10·01	. . .	0·47
S . . . . .	4·57	. . .	19·25

The speiss was roasted in heaps three times over, and then re-smelted in the same way, with 5 per cent. arsenical pyrites, 12·5 per cent. heavy spar, 50 per cent. slag from copper refining, and 50 per

cent. slags from lead matting, into a second speiss and matte. Of these the compositions are :—

	Speiss.	Matte.
Ni . . . . .	35·13 . . . .	4·37
Cu . . . . .	17·18 . . . .	37·45
Fe . . . . .	8·41 . . . .	12·68
Pb . . . . .	6·59 . . . .	22·81
As . . . . .	18·65 . . . .	trace
Sb . . . . .	10·82 . . . .	trace
S . . . . .	2·16 . . . .	24·48
Co . . . . .	10·70 . . . .	—

The speiss was disposed of to cobalt works.

When nickel is to be extracted from iron sows, they may be subjected to a blast in small refining hearths, and the iron oxide resulting slagged with quartz. In this way alloys are ultimately produced containing much nickel and copper; the method was formerly in use at Klefva in Sweden. Or by using the blast on a small hearth, and strewing nickel, coarse matte or nickel ore on the mass, the nickel will be obtained in a matte. This was practised formerly at the Ringeriges Works in Norway.

At one works in Saxony,<sup>1</sup> iron sows are treated, which contain molybdenum, the composition being 80 per cent. of Fe, 2·5 per cent. of Cu, 2 per cent. of Ni, 1·5 per cent. of Co, 6 per cent. of Mo, 8 per cent. of S. After being broken small they are roasted in a reverberatory furnace and then subjected to oxidising smelting in a similar furnace with quartz as a slagging material; in this way the greater part of the iron is slagged off, and a regulus is obtained, rich in molybdenum, nickel and cobalt. This latter is heated to redness in a reverberatory with saltpetre and soda, so as to form alkaline molybdates. These are removed by lixiviation, and the residue consists chiefly of a mixture of oxides of nickel, cobalt and copper. This is smelted into a speiss with arsenical pyrites.

## II. EXTRACTION OF NICKEL IN THE WET WAY

The wet way is especially used at present to extract pure nickel or nickel oxide from speiss and matte containing copper and cobalt. It is most unusual to submit ores directly to such a process, for it is usually cheaper to concentrate the nickel first in the dry way, forming

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 213.



a speiss or matte. This is especially true of ores containing sulphur and arsenic. A great variety of methods have recently been proposed for extracting nickel in the wet way from the ores in which it occurs as silicate (garnierite), though very few of these seem ever to have been applied. At present it still seems more profitable with these ores to concentrate the amount of nickel, even although not very high, and to form a matte in the dry way.

We distinguish then :—

A. Extraction of nickel directly from the ores.

B. Extraction of nickel from smelting products.

### A. EXTRACTION OF NICKEL DIRECT FROM THE ORES

If the ores contain arsenic or sulphur they must be roasted before being treated with solvents. (Sulphuretted ores may be prepared for a wet method by smelting with potassium carbonate and sulphur, as at the Gap Mine, Pennsylvania.)<sup>1</sup> Ores such as garnierite, containing nickel silicate, can be treated direct with solvents. Hydrochloric acid is generally the one used, occasionally dilute sulphuric acid. The latter, however, causes the formation of a precipitate of calcium sulphate afterwards, during the treatment of the solution with carbonate of lime and milk of lime.

Ferric sulphate has been suggested by Emmens<sup>2</sup> (Gossan process) as the solvent for the sulphuretted ores of Canada. According to him the nickel in Canadian pyrrhotite is dissolved out by this reagent, even from the unroasted ore, but the solution of nickel from the roasted ore seems to be very much more rapid. Emmens therefore suggests the roasting of the ore in furnaces, or the weathering of it, and subsequently treating it with ferric sulphate in wooden vats. Nickel is to be precipitated from the liquor as hydrate. The process has not yet been put into practice.

This process has been tried experimentally by the Canadian Copper Company, but not brought into definite use. In the most favourable cases only one-third of the amount of nickel and two-thirds of the copper of the ore are brought into solution by ferric sulphate.<sup>3</sup>

Macfarlane proposed to convert the nickel of the Canadian sulphuretted ore into chloride by roasting with common salt, and to

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1877, p. 300.

<sup>2</sup> *Mineral Industry*, 1892, p. 355.

<sup>3</sup> *Mineral Industry*, 1894, p. 463.

leach the product with water to dissolve this chloride. Iron was to be precipitated from the liquor by a small quantity of caustic soda, and any copper present by sodium sulphide. Finally the nickel was to be precipitated as hydrate by caustic soda. But nothing is as yet known with regard to the extent to which this method is put into practice.

Ricketts<sup>1</sup> brings nickel and copper into solution as sulphates, and then precipitates the nickel as basic sulphate by alkalies and alkaline sulphates. The basic sulphate is converted into monoxide by strong heating. Then the copper remaining in solution can be deposited electrolytically.

Richardson<sup>2</sup> converts both nickel and copper into chlorides, and separates the two salts by fractional distillation in an atmosphere of hydrochloric acid gas.

The way in which the solution is generally treated is as follows :—

It is first treated with sulphuretted hydrogen or an alkaline sulphide to precipitate copper, bismuth, lead, arsenic and any metals precipitable by these reagents. Then it is treated with chloride of lime to convert the iron into peroxide, which is precipitated by calcium carbonate. With the iron any arsenic present is got rid of as iron arseniate. Next comes the separation of cobalt as sesquioxide by chloride of lime. Finally the nickel is precipitated as nickelous hydrate by milk of lime or soda. The hydrate is converted into oxide by heating to redness, ground up fine, and treated with dilute acid to remove excess of chalk and calcium sulphate.

If copper is to remain with nickel, and an alloy of the two finally produced, the liquid can be treated at once with calcium carbonate, after previously oxidising the iron, and thus removing arsenic and iron. This is as long as the metals of the sulphuretted hydrogen group, other than arsenic, are absent.

Occasionally the nature of the ore renders modifications of these processes necessary. Further, special plans have very recently been elaborated for the treatment of nickel silicate, garnierite in particular, but have come to a very small extent into practical use, and therefore can only be mentioned shortly.

Grosse-Bohle<sup>3</sup> proposes to precipitate nickel and cobalt from their chloride or sulphate solutions by zinc, the temperature of the solutions being near their boiling point. Copper is removed by iron

<sup>1</sup> American Patents of October 3, 1893, and February 6, 1894.

<sup>2</sup> American Patent, April 10, 1894.

<sup>3</sup> German Patent, No. 97114.

before this precipitation, which is said to be unaffected by the presence of iron salts.

Formerly arsenical ores of nickel were worked by the wet method in Hungary<sup>1</sup> and in Bohemia; it is now no longer used for these ores. The ores were treated with hydrochloric acid after preliminary roasting (Louyet's process), and the solution was diluted with water, to precipitate the bismuth as basic chloride. Then chloride of lime was added, to oxidise ferrous oxide and arsenious oxide, after which milk of lime precipitated ferric hydrate and arseniate. Copper was precipitated by sulphuretted hydrogen or sulphide of barium, then cobalt as sesquioxide with chloride of lime, and lastly nickel hydrate by milk of lime.

At Joachimsthal<sup>2</sup> in Bohemia the silver ores containing from 5 to 10 per cent. of nickel and cobalt were formerly roasted in a current of steam. Silver was then separated as metal and nickel, and cobalt arseniates were formed. The roasted product was first treated with dilute sulphuric acid, and then with hot nitric acid. The former dissolved nickel and cobalt arseniates, the latter the silver and the remaining cobalt and nickel. After the silver had been precipitated by common salt the nitric acid solution was mixed with the sulphuric acid solution, and the whole treated with ferric chloride to convert the arsenic into ferric arseniate. Powdered limestone caused the precipitation of ferric arseniate, and from the solution remaining cobalt and nickel were successively thrown down by chloride of lime and milk of lime respectively.

Special proposals to separate nickel from silicates (garnierite and rewdanskite) are as follows:—

Herman<sup>3</sup> heats rewdanskite with sulphuric acid in stoneware vessels until the acid begins to vaporise, lixiviates the mass, oxidises the iron with salt and saltpetre, precipitates it by chalk, and precipitates nickel sulphide by sodium sulphide. This is completely roasted and the monoxide reduced.

Laroche<sup>4</sup> treats garnierite with its own weight of sulphuric acid 56° to 60° B., washes the solid product with warm water, and adds ammonium sulphate in quantity equivalent to the nickel sulphate present, and thus separates crystals of nickel-ammonium sulphate from the solution by evaporating down and cooling. These are dissolved in boiling water, and nickel carbonate precipitated by

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1849, p. 800.

<sup>2</sup> Kerl, *Metallhüttenkunde*, p. 554.

<sup>3</sup> *Berg- und Hüttenm. Ztg.*, 1876, p. 308.

<sup>4</sup> Wagner, *Jahresberichte*, 1879, p. 235.

solution of soda. Instead of ammonium sulphate, an equivalent quantity of alkaline oxalate may be added, and nickel oxalate thrown down from the solution. The precipitate is treated with boiling soda solution at about  $110^{\circ}$  C., when nickel carbonate is formed together with the alkaline oxalate. The carbonate is reduced to metal and the oxalate is used over again.

Rousseau<sup>1</sup> dissolves the mineral in hydrochloric acid, oxidises the iron with chloride of lime and precipitates it with calcium carbonate. Then he precipitates nickel with milk of magnesia. The solution remaining, consisting of magnesium and calcium chlorides, is evaporated down and he proposes to obtain hydrochloric acid and magnesia from the solid residue by heating in a current of steam.

Kamienski<sup>2</sup> dissolves the ore in dilute hydrochloric acid, oxidises the iron by a current of chlorine, precipitates it with magnesium carbonate, and decants off the warm liquid, and precipitates most of the nickel as carbonate, with soda. Then the solution is again treated with soda in the cold to precipitate magnesia and the rest of the nickel. The solution containing sodium and magnesium chlorides is evaporated down until salt crystallises out. From the remaining liquid magnesium chloride can be separated by evaporation; the latter salt will yield hydrochloric acid if heated to  $150^{\circ}$  in a current of steam.

Araud<sup>3</sup> mixes the ore into a paste with hydrochloric acid, and heats this in fireproof retorts until the chlorides formed volatilise. They are condensed and dissolved in water. From the solution iron is precipitated by calcium carbonate, and then nickel by milk of lime.

Sébilot<sup>4</sup> has suggested two methods. One is to mix the ore with sulphuric acid and ammonium sulphate, to add water and allow nickel to crystallise out of the solution as sulphate. The crystals are redissolved and nickel precipitated from this solution in the usual way. The second way is to heat the ore with sulphuric acid in a reverberatory furnace, to leach the solid mass remaining with water, precipitate iron by calcium carbonate after oxidising with chloride of lime, then to precipitate magnesium by sodium phosphate, and finally allow nickel sulphate to crystallise out of the lye.

Dixon<sup>5</sup> smelts the ore to a speiss and treats this in the wet way to be subsequently described.

Allen treats the powdered ore with sulphuric acid in the cold, adding some Chili saltpetre; then heats the mass to redness, lixiviates

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 260.

<sup>2</sup> *Loc. cit.*, p. 260

<sup>3</sup> *Loc. cit.*, p. 260.

<sup>4</sup> *Ibid.*

<sup>5</sup> *Loc. cit.*, 1879, p. 395.

with water, precipitates first iron and chromium by calcined magnesia, then nickel as sulphide by sulphuretted hydrogen. The sulphide is completely roasted and reduced.

Christoffe<sup>1</sup> has suggested several methods of treating garnierite in the wet way. These all appear to consist chiefly in the smelting of the ores to a matte and treating this as will be subsequently described.

The processes for direct wet treatment of the ore were as follows :—

1. The powdered ore is leached first with dilute, then with strong hydrochloric acid. Iron is precipitated from the solution in strong acid by quicklime or chalk, and then nickel by milk of lime.

2. The powdered ore is heated with concentrated oxalic acid solution which leaves nickel undissolved. The residue is reduced to obtain nickel. To recover the oxalic acid, the solution is treated with milk of lime and calcium oxalate thrown down, from which oxalic acid is separated by sulphuric acid.

3. The ore is treated with hot concentrated hydrochloric acid, chloride of lime added to the solution, containing excess of acid, to oxidise the iron; nickel oxalate is precipitated by oxalic acid, and the precipitate washed and heated.

4. The ore is treated with hot concentrated hydrochloric acid, chloride of lime is added to the acid solution, iron and aluminium are precipitated by calcium carbonate, nickel is precipitated as sesquioxide by lime-water and chloride of lime.

5. The ore is treated with concentrated hydrochloric acid, iron and aluminium are precipitated by the method of (4), magnesium chloride is added (if not already present in sufficient quantity), and nickel is precipitated with a small quantity of magnesia by quicklime. The precipitate is washed, dried, mixed with carbon, and heated to a very high temperature, when the sulphur is taken up by the magnesia. The nickel then forms in grains and is washed out of the ignited residue.

Herrenschmidt<sup>2</sup> has brought out a process which is said to be in use at the works of the Malétra Chemical Company at Petit Querilly, near Rouen, France. An ore from New Caledonia is employed, with 18 per cent. of manganese dioxide, 3 per cent. of cobalt monoxide, 1.25 per cent. of nickel monoxide, 30 per cent. of ferric

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 259; 1879, p. 138; Wagner, *Jahresberichte*, 1878, p. 233.

<sup>2</sup> *Pelleton, Genie Civil*, 1891, vol. xviii., p. 373; *Eng. and Min. Jour.*, 1891, vol. lii., No. 14.

oxide, 5 per cent of alumina, 2 per cent. of limestone and magnesia, 8 per cent. of silica. It is treated with a concentrated solution of green vitriol, which is said to dissolve manganese, cobalt and nickel as sulphates, while ferric oxide remains in the residue. The liquid after being separated from the residue and allowed to settle is treated with sodium sulphide which precipitates cobalt, nickel and a small quantity of manganese, as sulphides. The last can be removed from the precipitate by solution of ferric chloride. The solution containing manganese is converted into calcium manganite by treatment with milk of lime in excess and a current of air. This calcium manganite is utilised in the production of chlorine for making chloride of lime (Weldon process). The precipitate which has been freed from manganese, and contains only sulphides of nickel and cobalt, is subjected to roasting in a reverberatory furnace which converts it into a mixture of sulphates. These are dissolved in hot water and then converted into soluble chlorides by calcium chloride. For the separation of the metals, the liquid is divided into two parts. From the first part, they are precipitated as hydrates of protoxides by milk of lime, the precipitate is filtered off, washed into water, and the liquid treated with a current of chlorine and air until the sesquioxides are formed in it. The other half of the solution of chlorides is now added to this sesquioxide precipitate, and steam blown through the liquid for some time. Cobalt sesquioxide remains undissolved, while nickel sesquioxide passes into solution as chloride, and an equivalent quantity of cobalt sesquioxide is precipitated. After the whole of the cobalt has thus been separated, or else the whole of the nickel has gone into solution, the liquid is separated from the residue, and nickel is precipitated from it in the usual way by milk of lime.

Nothing is known yet as to the economic results of this process, which seems rather complicated, and capable of being conveniently put into practice only at Leblanc soda manufactories, which also make chloride of lime.

By the process patented in Germany,<sup>1</sup> Herrenschildt precipitates iron and copper from the solution containing iron, copper, cobalt, and nickel, as sulphates or chlorides, thus:—he precipitates the iron by copper carbonate, and then, after separating this precipitate, the copper by nickel hydrate or nickel carbonate. Lastly cobalt and nickel are obtained from the solution as described above, after this last precipitate has been removed.

Storer<sup>2</sup> proposes to digest garnierite in a finely divided condition with ferric chloride, the process being carried out in a closed vessel.

<sup>1</sup> Ger. Pat., No. 68,559.

<sup>2</sup> Ger. Pat., No. 100,142.

at a temperature of 187° C. After 5 to 6 hours' heating the nickel is said to go into solution as chloride, and the iron to be left as oxide. The latter may be used as a pigment, and the nickel solution treated for metal.

## B. EXTRACTION OF NICKEL FROM SMELTING PRODUCTS

These processes are divided into three groups—those for matte, those for speiss, and those for slags.

### 1. EXTRACTION OF NICKEL FROM MATTE

Matte, whether unroasted or dead roasted, will dissolve in acids. If unroasted matte is treated with acid, copper sulphide remains behind, and iron, nickel and cobalt dissolved for the most part. It is not possible to remove the whole of the cobalt and nickel from the residue, so that the latter has still to be specially treated for these two metals.

The treatment of unroasted matte with acid is therefore not to be recommended; it is undertaken only exceptionally. The usual method is to roast the matte dead before treating it with acids.

As ignited ferric oxide dissolves very slightly in dilute acid, it is well to raise the temperature as high as possible at the end of the roasting, so that as much iron as possible may remain in the residue. Hydrochloric or sulphuric acid is used as a solvent, the former preferably. If the roasting has been successful, practically no iron dissolves in either acid. Any arsenic present remains in the residue, as ferric or copper arseniate.

The usual method of treating the solution, subject to many variations, is the following:—It is treated with sulphuretted hydrogen or an alkaline sulphide to separate copper, lead, &c. Then iron is oxidised by chlorine or chloride of lime, and precipitated by calcium carbonate. This precipitation must take place in the cold, as above 40° C. an appreciable quantity of cobalt separates out. If copper has not been thrown down as sulphide, part of it now separates as carbonate. If arsenic acid is present it comes down with the iron.

Cobalt is next separated as sesquioxide by chloride of lime. Excess of chloride of lime throws down nickel as well. Potassium nitrite<sup>1</sup> throws down cobalt from a solution neutralised by potash and acidified again by acetic acid, as cobalt-potassium nitrite, and leaves nickel in solution; but it cannot be used to separate cobalt

<sup>1</sup> *Pogg. Ann.*, 74, 115; 110, 411; and *Ann. Chem. Pharm.*, 96, 218.

when lime or other alkaline earths are present, for then nickel is precipitated with the cobalt as nickel-potassium-calcium nitrite  $K_2CaNi(NO_2)_6$ .

If great quantities of cobalt are in solution, and extreme purity of metal is not essential, ammonium sulphate can be used to separate cobalt and nickel. This produces a difficultly soluble double salt with nickel sulphate, and an easily soluble one with cobalt sulphate. When the solution is sufficiently concentrated by evaporation, the nickel double salt separates out and leaves the cobalt in solution. The former is converted into nickel monoxide by heating, ignited with soda and saltpetre, and lixiviated. In the heating of the double salt ammonium sulphate can be recovered. Cobalt is precipitated from the remaining solution of cobalt-ammonium sulphate by ammonium sulphide. Cobalt sulphide is roasted, heated with saltpetre and soda and sent into market as sesquioxide.

From the solution, from which cobalt has been thrown down as sesquioxide by chloride of lime, nickel is precipitated as hydrate or as carbonate by milk of lime or by soda. The precipitate is filtered from the liquid in conical linen bags, and, if calcium sulphate is present, heated with soda, so that calcium carbonate and sodium sulphate are formed. The latter is washed out of the product by water, and the calcium carbonate removed by dilute hydrochloric acid. The decomposition of calcium sulphate by soda can also be conducted in the following way: the precipitate is heated with soda solution, the soda being present in excess, and then the residue of calcium carbonate is washed out with water acidified with hydrochloric acid. If hydrochloric acid has been used as solvent for the nickel, lime can be leached out from the calcined nickel monoxide with the same acid.

The nickel monoxide obtained in this way is reduced to nickel by the usual method.

De Coppet<sup>1</sup> proposes the treatment of roasted iron-free matte with a certain amount of sulphuric acid in order to obtain the copper as sulphate, mixed with a little nickel and cobalt salts. The residue consisting of the oxides of nickel, cobalt and copper is reduced to these metals by heating with carbon, and then treated with part of the copper sulphate solution. The cobalt goes into solution and an equivalent amount of copper is precipitated. After separating this cobalt solution, the residue of nickel and copper is treated with the remaining copper sulphate solution. This dissolves the nickel and an equivalent of copper is thrown out of solution. In the

<sup>1</sup> Ger. Pat., No. 64,916.



way cement copper and nickel sulphate solutions are obtained, and the latter may be worked for nickel. Nothing is known of the application of this process.

A direct treatment of matte with acid was formerly in use at the Scopello Works in Piedmont.<sup>1</sup> The nickel matte, containing 24 per cent. of Ni, 6 per cent. of Co, 12 per cent. of Cu, 23 per cent. of Fe, and 35 per cent. of S, was treated with hydrochloric acid (33 per cent. of HCl) in stoneware vessels surrounded with water in wooden barrels. Sulphuretted hydrogen was emitted from a tube in the cover of the vessel and was burned. After the matte had been three times treated with acid the liquid was syphoned off from the residue, which consisted of the copper sulphide of the matte and an appreciable quantity of nickel and cobalt sulphides. This was charged into the blast furnace during the smelting of matte or ore. The solution, containing chlorides of iron, nickel and cobalt, was first allowed to settle, and then evaporated to dryness in a cast-iron pot heated from above. The residue after this evaporation, a pulverulent mixture of the three lower chlorides, was heated in a reverberatory furnace for 3 or 4 hours, with continual stirring, during which process part of the iron volatilised as chloride, part remained as ferric oxide. After this treatment the mass was put into a vat with water, and then the remaining iron was oxidised by chloride of lime and precipitated by powdered marble. When the solution was clear, cobalt was thrown down by chloride of lime, nickel by milk of lime. The precipitates so obtained, cobalt sesquioxide and nickelous hydrate, were washed in woollen sacks until ammonium oxalate caused no cloudiness in the wash water. Then the two oxides were heated for 12 hours, and afterwards washed with acidified water.

The treatment of roasted matte with acids used to be carried on at the Isabella Works at Dillenburg, at the Victoria Works in Silesia, at Schneeberg in Saxony, and at the Christoffe Works at St. Denis.

At the Isabella Works nickel was produced in the wet way between 1848 and 1857; from 1857 to 1860 both nickel and the copper-nickel alloy. The methods for each are briefly described below.<sup>2</sup>

(a) In the earlier process the red-hot concentrated matte was quenched in water to render it brittle, then pulverised, and sieved. The powder, in quantities of 3 cwt., was subjected to roasting in a reverberatory furnace in order to remove sulphur and oxidise iron.

The roasted product was mixed to a thick paste with sulphuric acid (60° B.) in vats, and then gently heated for two hours in a rever-

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 229.

<sup>2</sup> *Schnabel, Preuss. Zeitsch.*, 1865, p. 109.

beratory furnace, during which time any ferrous sulphate was converted into ferric, and any excess of acid was driven off. The dry mass was treated with water to dissolve the sulphates, the solution then containing iron, copper and nickel sulphates. The first step was to precipitate iron and copper by calcium carbonate. For this purpose the liquid was raised to the boiling point in a copper boiler, and finely powdered calcium carbonate added by ladles full, by which iron and copper were thrown down as basic carbonates, and calcium sulphate with them. As iron comes down before copper, the precipitant was added only as long as iron was present in the solution, and then this precipitate, containing both iron and copper, was removed. A little nickel was always thrown down with copper, but in this way the presence of nickel in the first precipitate was avoided. It consisted only of iron and copper basic carbonates with calcium sulphate, and could be worked up into copper matte or copper. The filtrate from this precipitate was boiled up with a fresh quantity of calcium carbonate, and thus copper thrown down with a small amount of nickel. This precipitate was added in the concentration of nickel matte. The filtrate was treated with milk of lime to precipitate nickel hydrate. To remove calcium sulphate from this precipitate it was dried and heated with soda in fire-clay crucibles, whereby calcium carbonate and sodium sulphate were formed. The latter was washed out by water, the former by hydrochloric acid. The nickel monoxide was reduced in the usual way, and formed cubes with the composition :—

Ni . . . . .	98.29 per cent.
Cu . . . . .	0.24 „
Fe . . . . .	0.81 „

(b) According to the later method a coarse matte of average composition :—

Ni . . . . .	13 per cent.
Cu . . . . .	19 „
Fe . . . . .	35 „
S . . . . .	33 „

was converted into a concentrated matte of average composition :—

Ni . . . . .	24 per cent.
Cu . . . . .	39 „
Fe . . . . .	12 „
S . . . . .	25 „

This latter by oxidation under a blast on a hearth produced a matte composed of:—

Ni . . . . .	35 per cent.
Cu . . . . .	43     ,,
Fe . . . . .	2     ,,
S . . . . .	20     ,,

This last matte was dead roasted, and treated first with hydrochloric, then with sulphuric acid. The former dissolved the greater part of the copper and nickel, but not any iron present as ferric oxide; the proportion of the metals dissolved was 7 parts copper to 1 nickel. Both were precipitated from the solution by milk of lime. The precipitate was compressed, dried, and reduced to copper-nickel alloy, after the removal of the calcium sulphate.

The residue after treatment with hydrochloric acid (about 40 per cent. of the roasted matte) was twice treated with sulphuric acid in the way described above, whereby the greater part of the remaining copper and nickel and a portion of the iron passed into solution. The residue finally remaining was re-roasted. Iron was precipitated from the solution by calcium carbonate at a temperature of 55° C., and then copper as basic carbonate at 70° C. by the same agent. A little nickel accompanied this copper, increasing in amount with the amount of copper. In order to make this quantity of nickel as small as possible, it was sought always to dissolve as much copper as possible in the first treatment with hydrochloric acid.

The precipitate of basic carbonates of copper, nickel and iron was dissolved in hydrochloric acid. Copper and nickel were precipitated from this by milk of lime. This precipitate was first purified and then reduced to copper-nickel alloy. From the sulphuric acid solution still remaining, containing nickel sulphate with a little copper sulphate, the same agent—milk of lime—precipitated nickel hydrate, which was filtered off, compressed, and then dried.

The removal of calcium sulphate from these oxides (the copper oxide containing 8 per cent., the nickel monoxide 15 per cent.) was achieved by washing them with dilute hydrochloric acid after very strong heating. This acid removed the calcium sulphate, but no nickel monoxide, and very little copper oxide if the heating has been carried to the necessary temperature. After the acid had been used for washing, any portion of either metal present was removed from it by precipitation with milk of lime. This precipitate served to neutralise acid solutions which were about to be treated with calcium carbonate.

The oxides were reduced to metal in the usual way. The reduction of the nickel monoxide required 3 hours in time and a strong white heat, while that of the copper oxide containing a little nickel was accomplished at a lower heat in an hour and a half.

Metallic nickel was sent into the market in cubes; the cubes of the copper alloys were melted on refining hearths, taken off in discs, and sold in that form to the makers of German silver. At a later period the mixed copper and nickel oxides were reduced on a refining hearth with two tuyeres, and a copper-nickel alloy with 73 per cent. of nickel obtained.

The metallic nickel obtained in this way had the following composition :—

	I.	II.
Ni . . . . .	96.29	96.17
Cu . . . . .	0.41	2.17
Fe . . . . .	0.98	0.45

The refined copper obtained from the residues containing copper (from the solution of the precipitates in hydrochloric acid) had the following composition :—

	Ni.	Fe.	Cu.
The middle disc of the hearth . . . .	0.99	0.99	98.82
The lower disc of the hearth . . . .	0.44	0.80	99.06

Genth made the observation that the small black crystals that form on the upper discs in the hearth during the refining consist of nickel monoxide.

At the Victoria Works in Silesia<sup>1</sup> the concentrated nickel matte was dead roasted, then part of the copper oxide leached out with warm dilute sulphuric acid, and then the residue, washed, dried, ground fine and roasted, was reduced to a copper-nickel alloy containing 80 per cent. of nickel. Any nickel in the sulphuric acid solution was thrown down by copper oxide, and the solution was used to produce blue vitriol.

At Schneeberg, in Saxony, hydrochloric acid was used, instead of sulphuric, to dissolve copper oxide and sulphate out of the roasted matte. The method of working up the residue was the same as at the Victoria works.

At the Christoffe Works at St. Denis,<sup>2</sup> the matte obtained by smelting garnierite with gypsum was ground, roasted repeatedly in long-bedded calciners about 33 ft. long, and then treated with

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1877, p. 300; 1878, p. 245.

<sup>2</sup> *Knab, Metallurgie*, p. 560.

hydrochloric acid in stoneware vessels holding about 19 gallons standing in a water-bath. The action was increased by heating this water by steam. The solution was poured into wooden vessels, in which iron was first oxidised, then precipitated by calcium carbonate. Air was blown through to help the action, and served also to agitate the whole mass. It was transferred to larger wooden vessels in which the precipitate settled, and then the clear liquid was drawn off into other vessels in which nickel was precipitated by milk of lime. The hydrate was dried, washed, dried again, and then reduced to metal.

## 2. EXTRACTION OF NICKEL FROM SPEISS

The speiss is roasted dead, and then treated in the same way as dead roasted matte. In this roasting carbonaceous matter is mixed with the material to ensure the removal of arsenic.

At the George Works at Dobschau, in Hungary,<sup>1</sup> speiss of the composition:—

Ni	. . . . .	37	per cent.
Co	. . . . .	13	"
Cu	. . . . .	2	"
Fe	. . . . .	9	"
As	. . . . .	38	"
S	. . . . .	1	"

was stamped, and then roasted in wood fired reverberatory furnaces in quantities of 6 cwt. The time of roasting was 12 to 14 hours. At the end of this time 65 to 90 lbs. of sawdust or coal dust were added to the roasted product, which reduced the arsenic acid formed to arsenious acid and arsenic. The latter burns again to trioxide. The roasted product was then treated with sulphuric acid. From the liquid thus obtained, iron and part of the copper were precipitated by boiling with calcium carbonate. Cobalt sesquioxide was then thrown down by chloride of lime, and nickel hydrate by milk of lime. These oxides are dried, washed with acidified water, ground and sold to the smelting works in Saxony.

At Saint Benoit, near Liege,<sup>2</sup> speiss containing 45 per cent. of nickel was treated with concentrated hydrochloric acid at 80° C. Iron was precipitated from the solution in the usual way, and then copper by calcium sulphide. Next cobalt was precipitated by chloride of lime, and lastly nickel by milk of lime.

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 229.

<sup>2</sup> *Loc. cit.*

Dixon,<sup>1</sup> whose process has not yet come into general use, smelts garnierite with the addition of arsenical materials into a speiss, which is then dead roasted, and treated with hydrochloric acid. Into this solution chlorine is led to oxidise the iron, and the latter precipitated by the careful addition of nickel monoxide. Then cobalt is obtained as sesquioxide by leading more chlorine through the liquid, and adding more nickel monoxide. The solution containing the nickel combined with chlorine is evaporated. The solid mass obtained is converted into nickel monoxide by strongly heating in a current of steam, or into metallic nickel by heating in a current of hydrogen. A little nickel is precipitated with the cobalt sesquioxide, and is to be removed by leaching it with dilute hydrochloric acid.

At the works in Birmingham, England,<sup>2</sup> the completely roasted speiss is treated with hydrochloric acid. Iron is first oxidised, then precipitated as arseniate by neutralising the solution and warming it; the methods of this oxidation and this neutralisation are not mentioned. Copper is then thrown down by sulphuretted hydrogen. Finally the usual precipitants are used for cobalt and nickel.

### 3. EXTRACTION OF NICKEL FROM SLAGS

In the dry method, slags containing nickel are added to the charge in the smelting of ores and mattes.

If such slags are obtained as by-products in the smelting of copper they can be directly treated in the wet way, or can also be smelted into a copper-nickel alloy, which can be subjected to wet treatment. The treatment of the slags can be carried on in the same way as has been described for silicate of nickel and magnesia.

In Mansfeld<sup>3</sup> the slags containing nickel from the refining of copper were smelted in a blast furnace into black copper. This was granulated, refined, and then treated with dilute sulphuric acid in the presence of air. The solution was fractionally crystallised: copper sulphate separated first, and after it had been removed the liquor was evaporated to a certain point, when a mixture of the sulphates of iron and copper crystallised out. Further concentration and crystallisation yielded a mixture of copper and nickel sulphates. (According to von Hauer, if there is excess of copper sulphate in the solution, this salt will first crystallise out pure, and afterwards a copper-

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1879, p. 395.

<sup>2</sup> Phillips, *Elements of Metallurgy*, p. 415.

<sup>3</sup> *Berg- und Hüttenm. Ztg.*, 1859, p. 371; 1860, p. 501; 1861, p. 67; 1862, p. 160; 1846, p. 58; 1865, pp. 146, 386.

nickel-cobalt sulphate of the formula  $\text{CuSO}_4 + (\text{Co}, \text{Ni})\text{SO}_4 + 21\text{H}_2\text{O}$ . If there is excess of either nickel or cobalt sulphate or of both, this compound will crystallise out first, and the excess of these two sulphates will remain in the mother liquor.)

The copper-nickel sulphate, if free from iron, was heated in a roasting furnace to remove sulphuric acid. The residue, consisting of oxides, was leached with water and dried, and then reduced in a Sefström furnace to an alloy with 40—68 per cent. of Cu, 30—59 per cent. of Ni, 1.1 to 1.8 per cent. of Co, 0.5 to 1.3 per cent. of Fe, and 0.07 to 0.34 per cent. of S. This was melted on a refining hearth of graphite, with two tuyeres, and taken off in discs.

Herter<sup>1</sup> has proposed to heat a complex sulphate, such as the above, but containing iron, in a reverberatory furnace, and to treat the mixture of oxides so obtained with dilute sulphuric acid, which will dissolve nickel and copper, but not iron. From the solution copper and nickel are to be precipitated by soda, the resulting basic carbonates heated to form oxides, and the latter reduced.

### III. EXTRACTION OF NICKEL BY ELECTROLYSIS

There has been no lack of suggestions for, and of experiments, on a large and small scale, upon the electrolytic production of nickel. The direct production of nickel from ores has not succeeded, in fact there is little likelihood of its doing so, since nickel ores are too impure and contain too little of the metal to be used as anodes, or to be dissolved in any other way within the circuit. The preparation of nickel solutions from ores outside of the circuit is difficult in the case of silicates, and expensive in the case of sulphur and arsenic compounds of nickel, owing to the impurities and the low nickel content; and in addition the sulphide ores always contain a portion of their nickel in the form of silicates hard to dissolve.

The electrometallurgical method can only be employed for the treatment of mattes and alloys; so far its use has been restricted to nickel-copper mattes and nickel-copper alloys, and its application has been greatest in the separation of nickel and copper, owing to the difficulty of accomplishing this in the dry way. It is most profitably employed to obtain nickel from its alloys with copper, since the conversion of nickel-copper mattes into alloys is not a costly process, and furthermore iron is eliminated in the preparation of the matte itself. Only meagre information has been so far published concerning the processes adopted.

<sup>1</sup> *Berggeist*, 1865, No. 20.

High potentials are necessary to deposit nickel from solution, and these cause most other metals to be precipitated. The decomposition tension of nickel sulphate is 2.09 volts, of the chloride 1.85 volts (Le Blanc). It is therefore very difficult to obtain a thick deposit of nickel. To accomplish this the electrolyte must be hot. The strength of current for thick deposits of nickel is shown by the results of experiment to be between 3.5 and 8.5 ampères per square foot, with a potential of 3 to 6 volts, according to the nature of the liquid. According to Borchers,<sup>1</sup> in using the salts of cresol-sulphonic acid and insoluble anodes, 5.5 ampères per square foot, and 2 to 2½ volts are necessary. According to Brand,<sup>2</sup> to deposit nickel from a solution of the sulphate saturated with ammonia, with a carbon anode, a potential of 2.4 volts, and a current of 2.8 ampères per square foot is necessary. The same potential is necessary if an iron anode is used instead. A current of 1 ampère separates 16.83 grains of nickel in an hour. To separate 1 kg. nickel in an hour, 914.9 ampères would be necessary. The energy necessary for this is

$24 \times 914.9 \text{ Watts} = \frac{2195.8}{75 \times 9.81} = \frac{2195.8}{735} = 2.99 \text{ h.p.}$ , or taking into account a 12 per cent. loss in the conversion of mechanical energy into electricity, and a 25 per cent. loss in the current (through conversion into heat, bad connections, &c.),

$$= \frac{2.99}{0.88 \times 0.75} = 4.48 \text{ h.p.}$$

At the rate of 2 kg. of coal for 1 h.p. per hour, 9 kg. coal will be necessary to deposit 1 kg. nickel from the solution described.

The loss of energy in the latest engines is considerably less than the above. The consumption of coal for one horse-power can be reduced in the newest steam engines to between 1 and 1.5 kg.

If nickel is to be separated from its mattes or alloys with copper, it is the copper which is deposited from an acidified electrolyte on the cathode, while the nickel passes into solution, because copper is deposited by a weaker current than nickel. After purifying the solution from other metals, especially iron, which may be precipitated by various reagents, nickel is deposited from the solution by the use of insoluble anodes.

In the year 1843 Dr. Böttger<sup>3</sup> recommended the double sulphate

<sup>1</sup> *Elektrometallurgie*, p. 103.

<sup>2</sup> Dammer, *Chem. Technologie*, vol. ii. p. 27.

<sup>3</sup> *Journ. für Pract. Chem.*, vol. xxx., p. 267.



of nickel and ammonium as electrolyte, and investigated, in a series of researches, the conditions under which nickel is deposited as a lustrous white metal. By the use of such electrolytes metal can be covered with a firmly adherent coat of nickel, but it is not possible to obtain it in a thicker deposit without the nickel becoming brittle.

Bischoff and Tiemann<sup>1</sup> obtained pure nickel electrolytically, for Winkler's determination of the atomic weight of the metal, as follows:—A solution of nickel sulphate was prepared containing 32.84 grams of nickel per litre. The electrolyte consisted of 200 cc. of this solution, 30 grams of ammonium sulphate, 50 grams of ammonia (of specific gravity 0.905) and 250 cc. of water. The cathode was a polished nickel plate 9.7 cm. long and 7.9 cm. wide, the anode a piece of platinum foil of the same dimensions. The E.M.F. was 2.8 volts, and the current strength 0.8 ampère. As soon as the nickel deposit had attained a certain thickness, it became detached in thin curly flakes from the cathode, and formed a white shining mass with a yellowish tint. The metal was pure, since repeated heating in an atmosphere of hydrogen failed to produce any loss of weight.

Förster's<sup>2</sup> experiments show that it is possible to obtain a compact nickel deposit of any desired thickness by the use of crude nickel anodes, provided the electrolyte be warmed to 50–90° C. (Classen<sup>3</sup> had previously recommended the use of a hot solution of nickel sulphate, neutralised with ammonia or potash and containing ammonium oxalate, in the electrolytic determination of nickel). Förster confirmed Böttger's observations that the electrolysis is best performed with solutions of the sulphate. The electrolyte consisted of a solution containing 145 grams of nickel sulphate (*i.e.* 30 grams of nickel) per litre; the anodes of stout nickel foil (containing 0.4 per cent of carbon, 0.02 of silicon, 0.10 of copper, 0.43 of iron, 0.14 of cobalt, and 0.02 of manganese) wrapped in parchment to hold back the anode slimes; and the cathodes of thin sheet nickel from which the deposit could be readily detached. The electrolyte was kept in motion during the experiments by bubbling air or carbon dioxide through it. Compact nickel deposits, light grey to tin white in colour, were obtained by electrolysis at 50° to 90° C. with current densities of 50 to 250 ampères per square metre (*i.e.*, 42 to 210 ampères per square yard). The higher the current densities, the

<sup>1</sup> *Zeit. für anorg. Chem.*, 1895, p. 8.

<sup>2</sup> *Zeit. für Elektrochemie*, 1897, 1898, vol. vi.

<sup>3</sup> *Quantitative Analyse auf electrolytischem Wege*. Aachen, 1882.

lighter and more lustrous were the deposits; unevenness of deposit, which with time gave rise to a warty surface, was shown to be due to adhering bubbles of hydrogen, which disturbed the even distribution of the current. This could be guarded against by keeping the electrolyte agitated, so that bubbles could not cling for long to the cathode surface.

In the main experiments the electrolyte contained 7000 grains of nickel per gallon, the temperature was  $60^{\circ}$  C., the current density 14 to 18 ampères per square foot, the tension of the bath 1.3 volt and the distance between the electrodes 4 cm. (*i.e.*, about  $1\frac{1}{2}$  inches). The deposit obtained under these conditions was a compact metal of great toughness. Carbon, silicon, copper, and manganese had been completely eliminated by the electrolysis, but three-quarters of the iron and cobalt of the anodes had been precipitated on the cathodes. This was not affected by a repetition of the process, so that it appears that both iron and cobalt are more electronegative than nickel. In agreement with this is the fact that electrolytic nickel generally contains a little iron. Small quantities of cobalt and iron (0.48 to 1.32 per cent.) do not affect the density and the lustre of nickel. Only when the quantity of iron is considerable does the nickel deposit break away from the cathode in large curled leaves.

If nickel chloride be used as electrolyte, the deposit is leafy at ordinary temperatures and in neutral solutions. Raising the temperature produces quickly a green powdery deposit of basic nickel chloride. It was found that this could be prevented by making the electrolyte slightly acid, 175 grains of hydrochloric acid per gallon sufficing for this purpose; so that for every grain of nickel precipitated 0.05 to 0.1 grain of acid had to be run in. The temperature in this case was  $50^{\circ}$  to  $90^{\circ}$  C., the current density  $6\frac{1}{2}$  to 28 ampères per square foot, and the electrolyte contained 3500 to 8400 grains of nickel per gallon; the deposit was dull grey to silver white and its lustre and toughness increased with the temperature and the concentration of the electrolyte. Bubbles of hydrogen formed more readily than in the case of the neutral sulphate solutions, and as a consequence the nickel showed more tendency to form warty deposits.

Förster's experiments on the electrolysis of chloride solutions, using anodes of carbon, gave unsatisfactory results. The electrolyte contained 7000 grains of nickel per gallon, the temperature was  $80^{\circ}$  C., the current density 18 ampères per square foot, the tension 1.8 to 1.9 volts, and the distance between the electrodes  $\frac{3}{4}$  inch. At first the deposit was lustrous and compact. Owing

however, to the solvent action of the liberated chlorine upon the nickel the yield was only 66–70 per cent., and soon fell to  $\frac{1}{3}$ – $\frac{1}{4}$  of the theoretical; at the same time darky carbonaceous particles appeared at the cathode, and the nickel deposit contained eventually 0.18 per cent. of carbon and was brittle. Förster regards this phenomenon as due to the passage of organic compounds from the anode-carbon into the electrolyte.

Wohllwill<sup>1</sup> has lately investigated the separation of copper from nickel in their alloys. The alloy is used as the anode and a solution of nickel and copper sulphates as the electrolyte, and the separation depends upon the solution of both metals and the precipitation of the copper only at a particular tension and current density. Now the diminution in concentration of the copper in the electrolyte, and the increase in concentration of the nickel, proceeds so quickly, that in a short time, not only copper but also hydrogen is liberated at the cathode, for the copper deposited at the cathode is equivalent to the copper and nickel dissolved at the anode. Hence more copper is deposited at one electrode than is dissolved at the other (1 lb. of nickel is dissolved at the anode for 1.08 lb. of copper precipitated at the cathode). To obtain therefore a compact deposit of copper, an amount of copper (in the form of sulphate) equivalent to the amount of nickel dissolved, must be added constantly or at intervals to the electrolyte. This addition is only stopped when the concentration of nickel sulphate in the electrolyte has reached the desired point. Practically, this concentration is not allowed to exceed 12½ lbs. of nickel sulphate per cubic foot, otherwise the cathode deposit is apt to enclose liquor. Much less energy is needed to decompose copper sulphate under these conditions than when a pure copper sulphate solution is electrolysed with insoluble anodes.

To obtain the nickel as sulphate from the solution, the method is to replace the old cathodes, as soon as the electrolyte has become sufficiently concentrated in nickel and too impoverished in copper to give a compact deposit, by new cathodes of copper or lead, upon which the copper is deposited in a less pure and compact form. Then the soluble anodes are replaced by insoluble ones, lead plates being used when the liquor is such that there is no possibility of the formation of lead peroxide. This is the case, according to Borchers, when the alloy contains some iron, and the electrolyte consequently some ferrous sulphate. If the electrolyte is free from iron (and if the water used has not been quite free from chlorides) then the lead

<sup>1</sup> Borchers, *Elektrometallurgie*. 3rd ed., 1902, p. 284.

anodes are speedily attacked. After the greater part of the copper has been removed from the electrolyte in this way, the mixed vitriols are won from it by evaporation and crystallisation, and these are freed from iron and copper by dissolving and precipitating with suitable reagents. The solution is then worked up for pure nickel vitriol by repeated crystallisation, or for nickel ammonium sulphate by addition of ammonium sulphate.

Günthner, whose experiments will be further described later on, found that the copper deposit in electrolysis was of good character, so long as the concentration of copper in the electrolyte did not fall below 1 per cent. He states also that nickel ammonium sulphate is but little suited for electrolysis, since its solution at the ordinary temperature contains too little nickel (1 per cent.).

Borchers<sup>1</sup> has proposed a method for the treatment of alloys of nickel, copper, and iron prepared from mattes. In his experiments the proportional quantities of these three metals in the alloy were as 2:1:1. The alloy was used as anode, and an acid solution of copper sulphate as electrolyte. Most of the copper was deposited on the cathode, while iron, nickel and some copper passed into solution. As soon as the liquor had become saturated with sulphate of iron and nickel, it was run off, the copper precipitated by scrap iron, and the iron and nickel separated by addition of ammonium sulphate in quantity equivalent to the nickel in solution, and by crystallisation of the double sulphate of nickel and ammonium at a density of solution below that needed for the crystallisation of iron vitriol. This double salt crystallises from a boiling hot solution at a density of 18° B., but ferrous sulphate and ferrous ammonium sulphate do not crystallise out until the density reaches 31° B. If the density of the liquor remains at least 5° B. beneath that requisite for the crystallisation of ferrous or ferrous ammonium sulphate, then crystals of nickel ammonium sulphate are obtained, which can be freed from iron-salt by re-crystallisation. If the nickel double salt is to be used for electrolytic purposes (though this is inadvisable, as stated above), then the crystals are washed, and dissolved, and the iron precipitated by chromates or persulphates.

Borchers converts the nickel ammonium sulphate into nickel sulphate, the solution of which is used as the electrolyte. This is brought about by double decomposition with nickel carbonate, obtained by the addition of soda to impoverished electrolyte, the products being nickel sulphate and ammonium carbonate. The

<sup>1</sup> *Jahrbuch d. Elektrochemie*, 1897, vol. iv. p. 305. *Elektrometallurgie*, 1903 p. 189.

plant employed in the preparation of ammonium carbonate from ammonium sulphate and soda may be used in this case too. As small quantities of iron are taken up, the solution of nickel sulphate must be purified by chromates or persulphates, before being used for electrolytic purposes.

Günther<sup>1</sup> has experimented on the extraction of nickel and copper from pyrrhotite containing these metals, the nickel being isolated finally as sulphate, and the solution of this electrolysed both with soluble and insoluble anodes. Lead plates were used as insoluble anodes, a solution of nickel ammonium sulphate containing 1 per cent. of nickel and 0.3 per cent. of acetic acid was the electrolyte, and sheet nickel was used for the cathodes. The temperature of the bath was 70° C., the current density 18 ampères per square foot, the tension at the beginning 3.5 volts, and the distance between the electrodes 6 to 7 cm. The nickel deposit was compact and smooth at first, but later a dark brown adhesive coating formed, and the E.M.F. rose to 5.6 volts after 8 to 10 hours, owing to the higher resistance of this deposit. It fell again to 3.5 volts when the brown coating was removed. The yield of metal did not exceed 35 per cent. of the theoretical.

The brown deposit was produced by the conversion of part of the anode lead into lead peroxide and lead sulphate. The former conducts well, but the crust formed by its enclosing lead sulphate has a high specific resistance. The poor yield in the experiments was probably largely due to the small concentration of the electrolyte, since sulphate solutions with 3 per cent. of nickel gave a yield of 70 per cent. of the theoretical. As however the concentration of nickel ammonium sulphate at the ordinary temperature does not exceed 1 per cent. of nickel and as the double salt crystallises out on cooling, it is obvious that this salt is unsuitable for electrolysis on a large scale. Hence it was replaced by nickel sulphate in the experiments with soluble anodes of lead, zinc, and copper.

In these experiments diaphragms were used, the electrolyte, a solution of nickel sulphate containing 3.5 per cent. of nickel, being allowed to flow through the cathode division, whilst in the anode division there was placed a solution of two salts, so selected that the anion of the first formed a soluble compound with the anode, and the anion of the other precipitated an insoluble compound of the anode metal from this soluble compound, regenerating at the same time the first salt. As metal is thus consumed constantly, it was

<sup>1</sup> *Auszug aus einer Inaugural-Dissertation für die Technische Hochschule Aachen in der Zeitsch. d. Vereins deutscher Ingenieure*, April 18, 1903, p. 574.

sought to obtain the metal in the insoluble compound, in the form of a pigment of some value.

In the experiments with lead anodes, the salt with the solvent anion was sodium chlorate, that with the precipitating anion, sulphate, chromate, or carbonate of sodium. The sodium chlorate solution contained 1·2 per cent. of the salt.

When sodium sulphate was employed, it was thought, that with the precipitation of nickel at the cathode, lead would dissolve at the anode as chlorate, and by reaction of this with sodium sulphate, lead sulphate would be precipitated and sodium chlorate regenerated; furthermore that sodium sulphate would be regenerated from equivalent amounts of the decomposition products of the nickel sulphate in the cathode division, and the sodium chlorate in the anode division. The experiments however showed, that though a good deposit of nickel was obtained with a yield of 95·4 per cent. of the theoretical, yet a perfect regeneration of sodium sulphate by no means took place, so that constant additions of this salt had to be made. Again, to keep the nickel of good quality, a constant supply of acid at the cathode was necessary. Electrolysis was therefore performed with electrolytes containing 0·02 to 0·4 per cent. of sulphuric acid, and the consumption of acid found to be 0·35 gram per ampère-hour. The best results were got when the electrolyte contained 0·03 to 0·06 per cent. of free acid.

When sodium chromate was used as the precipitant, the insoluble salt was a mixture of chromate and sulphate of lead. The nickel deposit was good; the yield 90 per cent. of the theoretical, the tension of the bath 2·5 to 4·2 volts, and the current density 16 to 28 ampères per square foot.

With sodium carbonate in the anode division, the precipitate was a mixture of carbonate and sulphate of lead. The nickel was of good quality and the yield was 95 per cent.; the tension was 1·5 volts and the current density 11 ampères per square foot.

When copper anodes were used, the solvent and precipitant were sulphate and carbonate of sodium respectively. The nickel deposit was fair, and the insoluble salt consisted of a mixture of copper carbonate and cuprous oxide.

In the experiments with zinc anodes, ordinary commercial metal was used; the solvent was chloride or sulphate of sodium, the precipitant soda. The products were zinc carbonate (coloured) and a perfect nickel deposit. The yield was 90 to 93 per cent. of the theoretical, the tension 2·3 to 2·6 volts, and the current density 31 to 36 ampères per square foot.

Although the nickel deposits are good in the experiments with soluble anodes, yet the precipitates of insoluble compounds are worthless as pigments. Hence the endeavour was made to obtain these bodies at the ordinary temperature outside of the electrolytic cell, the solvent salt being added to the anode division for this purpose. The metallic solution thus obtained was run off from the vessel and there treated with the precipitating salt. This method could only be of use when the soluble salt formed at the anode did not diffuse to the cathode and give up its metal along with the nickel. Now lead chlorate could not be detected in the liquor at the cathodes, and the nickel was of good quality. The lead could be run off from the bath yielded, on addition of sodium chromate, which could be utilised as a pigment, and sodium was regenerated. The zinc salt (sulphate and chlorate) was present in small quantity at the cathode, but none was thrown down with the nickel. The zinc liquors could be treated successfully with white or lithopone. The copper salt (sulphate or chlorate) was run off into the cathode division and was deposited along with the nickel, making the latter spongy.

Borchers<sup>1</sup> has devised an apparatus suitable for the electrolytic extraction of nickel. The diaphragms are clay cells 21 inches long, 11 inches high, and 5½ inches wide; these are supplied by the Royal Porcelain Manufactory in Berlin. The rest of the apparatus differs from that used in the electrolysis of copper.

It is still an open question whether the production of lead paints together is economically sound. There can be no doubt however in the case of zinc pigments, since the cost of zinc sulphate by the solution of zinc is much dearer than by the other methods for preparing it.

We shall now discuss other methods and proposals for the electrolytic extraction of nickel.

The extraction of nickel from its ores was tried at the Smalt Works in Silesia. Nickel was deposited by a current from an ammoniacal solution containing caustic soda. This method has not yet come into use.

Extraction of nickel from smelting products was proposed by André in 1877.<sup>2</sup> The substances containing nickel,—metals or alloys,—were to be cast into anode plates, and suspended in a solution of sulphuric acid. For the cathodes, copper or carbon plates were suggested. The current should be so regulated that only the nickel was separated out on the cathodes, while the other metals remained in the solution.

<sup>1</sup> *Elektrometallurgie*, 1903, p. 292.      <sup>2</sup> Ger. Pat., No. 6048, November 1877.

solved in the electrolyte. To remove the last portions of copper from this, a carbon anode should be introduced after the disappearance of the original one. Thus the last of the copper is deposited from the acid solution, which now should contain only nickel sulphate with some iron sulphate.

To remove the iron the solution should be made ammoniacal, and evaporated down in leaden pans in a current of air, so that the iron may be precipitated as ferric hydrate. The liquid filtered from this consists of nickel sulphate only, and may be worked up for the crystallised salt, or the monoxide, or metallic nickel. The last may be obtained by precipitating the hydrate or carbonate, and reducing as has been already described, under wet treatment, or the electric current may again be used. In the last case the solution is made ammoniacal. Carbon or nickel plates, or copper plates covered with graphite, are to be used as cathodes. Iron or zinc plates are recommended as anodes, so as to avoid polarisation.

It should be noticed, however, that iron or zinc is not adapted for the anode, as solutions of iron and zinc salts differ but slightly in electrochemical behaviour from those of nickel salts.

Stahl<sup>1</sup> proposes a similar method for extracting nickel from coarse copper. This is melted in a reverberatory furnace, the hearth of which is of basic material, and is oxidised to get rid of iron and arsenic, until nickel begins to pass into the slag. Then it is poled and cast into anode plates. These are to be subjected to electrolysis in order to separate the copper, sulphuric acid being the electrolyte, and sheets of copper the cathodes. The current is regulated so that only copper is deposited on the cathode from the acid solution, whereas nickel, iron and small quantities of arsenic pass into the solution, while silver, lead, antimonious acid, antimony oxide, arsenic acid and copper sulphide form a thick mud, which falls to the bottom of the liquid. The separation of the last portions of copper from the solution is performed with carbon anodes as in André's process. Fresh anodes may also be inserted as required in order to obtain by itself the copper which is rendered impure by simultaneously deposited arsenic.

Chloride of lime is next added to the warm solution containing iron and nickel, to convert ferrous into ferric sulphate; and then slight excess of soda is added to the acid solution, and this is heated until the whole of the iron is thrown down as basic ferric sulphate. This precipitate is removed by filter presses, and the liquid used to make nickel sulphate, monoxide or metal. If metal is to be deposited

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1891, p. 270.



by electrolysis, the solution is made ammoniacal; dense carbon forms the anode, a sheet of nickel or a sheet of copper, covered with graphite, the cathode.

If nickel monoxide is to be produced from the copper-nickel alloy, the copper is still deposited by electrolysis in the way described, and nickel dissolved. Then the monoxide is obtained just as in the wet treatment.

Hoepfner<sup>1</sup> proposes to obtain from the material containing nickel as produced by the previously described wet treatment a pure neutral solution of nickel; to acidify this with a weak, badly-conducting oxy-acid (such as citric or phosphoric acid), and then to electrolyse with an insoluble anode. The anodes dip into cells filled with a solution of the chloride of an electropositive metal. Vertically rotating or oscillating discs of metal are used as cathodes. The deposition of spongy material is prevented by movable brushes or rubbers. The electrolyte is kept in constant motion by pumps.

Instead of insoluble anodes, soluble or partially soluble ones may be used. The material for such can only be of metals which are more electropositive than nickel (such as zinc), and will not be deposited with the nickel. (These methods are proposed also for the extraction of cobalt, zinc, lead, tin, and copper.)

In a later patent<sup>2</sup> Hoepfner suggested smelting nickel and cobalt ores with copper ores, and treatment of the resulting matte as in his process for the electrolytic production of copper from its ores. The preparation of a nickel-copper matte in this way from nickel ores free from copper is against the principles of nickel and copper smelting, and is self-condemned in consequence. The method can claim consideration in the case of the treatment of copper-nickel mattes obtained from copper-bearing nickel ores. The method consists in the treatment of the pulverised matte with a mixture of solutions of copper and calcium chlorides, whereby the copper and nickel go into solution as sub-chlorides. The solution is purified from iron and then the greater part of the copper precipitated by electrolysis. The residual copper and the iron and other impurities are removed, and the nickel (and cobalt) are deposited electrolytically.

The copper chloride solution attacks the sulphide of copper and nickel, liberating sulphur and forming nickelous and cuprous chloride, an equivalent amount of cupric salt being reduced to cuprous salt. The nickel chloride is soluble in water, the cuprous chloride in the calcium chloride which is present.

<sup>1</sup> Eng. Pat., No. 13336 of 1893.

<sup>2</sup> Eng. Pat., No. 11307 of 1894.

The purification of the solution from iron may be performed with caustic alkali, or an alkaline carbonate, with the injection of a current of air.<sup>1</sup> After the greater part of the copper has been removed by electrolysis of the solution, bleaching powder is added to oxidise any ferrous to ferric salt, and the latter is precipitated by lime. Lead and copper may be removed either electrolytically or by means of sulphuretted hydrogen in special purifying vats. After the second purification the nickel is deposited by the electric current. In electrolysing solutions of cuprous chloride chlorine is liberated at the anode. This is utilised by causing a stream of cuprous chloride solution to flow round the anode, the chlorine being absorbed thereby and the cuprous salt oxidised to cupric salt. Chlorine is also liberated in the electrolysis of nickelous chloride, but this is led into a solution of cuprous chloride outside the bath; for if the anode were enclosed with a diaphragm, and if the cuprous solution flowed through this, as in the latter case, some copper solution would diffuse to the cathode and copper would be deposited from it along with the nickel.

The cupric chloride obtained in the electrolysis of cuprous and nickel chlorides is used for the solution of copper and nickel from the mattes. This process with certain modifications is said to be in use at Papenberg in East Friesland for the treatment of nickel-copper mattes.

A process has been suggested by the firm Basse and Selve in Altena,<sup>2</sup> which consists first in adding certain organic bodies to neutral or slightly acid solutions containing nickel, cobalt, iron, and zinc, such as will prevent the precipitation of their oxides by alkalies. Such are acetic acid, citric acid, glycerine and dextrose. Then the solution is made alkaline by soda or potash lye, and subjected to electrolysis. Thus iron, cobalt, and zinc are deposited on the cathode, while nickel either remains entirely in the liquid or comes down partly as hydrate, according to the strength of the alkaline solution. The precipitation of the hydrate occurs if the current is continued for long. The solution then contains nickel, free from the other metals, and ammonium carbonate is added to it in such a quantity as to form carbonate of all the free alkali; then it is subjected to electrolysis. Nickel is deposited on the cathode with a bright surface.

Nothing is known as to the practical introduction of this process. Rickets<sup>3</sup> proposes to separate nickel and copper by electrolysing

<sup>1</sup> Eng. Pat., No. 22030 of 1891.

<sup>2</sup> Ger. Pat., No. 64251 of 1891.

<sup>3</sup> U.S. Pat., February 6, 1894, No. 514276.

the solution of the salts of both metals, after addition of the sulphate of an alkali metal. The copper is deposited at the cathode and the nickel separates, with the increase of acid, and collects at the bottom of the bath as the sparingly soluble double sulphate of nickel and the alkali metal. This process gives no promise of success, and has never been put into practice.

Le Verrier's method<sup>1</sup> of separating iron and nickel, when ferriferous nickel is used as the anode, is as follows. The electrolyte is either nickel ammonium sulphate, or a weak solution of nickel ammonium chloride containing sodium chloride. By maintaining the bath slightly alkaline by means of the hypochlorite of an alkali metal or an alkaline earth, the iron, which is dissolved along with the nickel, is oxidised and precipitated in the bath, being thereby prevented from being deposited with the nickel at the cathode. This oxidation of the iron can also be effected by chloride of lime (bleaching powder), or if the quantity be small, by air. If the double sulphate be used as electrolyte, lime salts must not be added for oxidation purposes, since otherwise insoluble calcium sulphate will be formed. The oxidising agent in that case would be sodium hypochlorite.

Kugel<sup>2</sup> suggests the use of hot nickel salt solutions acidified with perchloric or perbromic acids or sulphuric acid, in order to obtain the nickel on electrolysis in a tough condition fit for rolling. The anodes are of nickel matte or of some insoluble material, and a suitable acid content (which depends mainly upon the current density) is maintained by the addition of a very strong solution of the magnesium salt of the acid in question, magnesium sulphate being employed for instance in the electrolysis of nickel sulphate. One gallon of water at 90° C. can hold in solution 56,000 grams of nickel sulphate and the same amount of magnesium sulphate.

Frasch's process<sup>3</sup> for the treatment of nickel-copper matte, which is said to have been tried experimentally by the Nickel Copper Co. in Ontario, is carried out as follows. The coarsely crushed matte is charged into a vat, on the bottom of which are copper plates used as anodes. A thin layer of sand covers the matte and serves as a diaphragm. A strong solution of salt is run into the vessel until it just covers the diaphragm, and upon this a weak solution of soda which forms the cathode division. Water may be used instead of soda, since the latter is produced during the course of the process. The cathodes are arranged in the water or soda solution. On

<sup>1</sup> Ger. Pat., No. 112890.

<sup>2</sup> Ger. Pat., No. 117054.

<sup>3</sup> *Eng. and Min. Journ.*, 1900, vol. lxx., p. 272.

electrolysing, the chlorine of the salt combines with the metals of the matte forming a solution of chlorides of nickel and copper, from which these metals may be deposited either chemically or electrolytically, and caustic soda is formed at the cathode. Another method of treating the solution of the chlorides is to precipitate part of the copper electrically, and to use the residual solution, which contains the copper as cupric chloride, for leaching matte, as in the Hoepfner process. This method has not come into use.<sup>1</sup>

Ulke<sup>2</sup> has described a direct method for the treatment of iron-free copper-nickel matte containing on an average :—

Cu .	43·4 per cent.	Ag .	6·72 ounces per ton
Ni .	40·0 „	Au .	0·96 to 1·92 ounces per ton
Fe .	0·3 „	Pt .	4·8 „ „
S .	13·8 „		

The matte is cast into anodes and the cathodes are made of sheet copper. The baths are arranged with air-circulation apparatus as in the refining of sugar. The electrolyte is a solution of nickel sulphate obtained by dissolving the granulated matte in dilute sulphuric acid, and adding 8 per cent. of free acid to the solution. About 0·5 per cent. of ammonium sulphate is also added to prevent the precipitation of arsenic, and a little hydrochloric acid to keep the silver in the anode slimes. The strength and tension of the current are so selected that the copper is deposited at the cathode, the nickel is dissolved, and the precious metals collect in the anode slimes. After the complete solution of the copper at the anode and the precipitation of the greater part at the cathode, the electrolyte is run off, the residual copper thrown out by sodium sulphide or by filtering through nickel matte, and the iron removed as hydroxide by the addition of freshly precipitated nickel hydroxide, as in Cabell Whitehead's method. After filtration the nickel may be recovered from the solution by electrolysis, by crystallising out its vitriol, or as carbonate by the addition of soda, the carbonate being afterwards converted into oxide.

If electrolysis is resorted to, the liquor is made neutral or faintly ammoniacal, and the process is carried out with anodes of carbon or lead and cathodes of sheet nickel, if the object be to obtain the nickel free from copper. If there be no objection to the presence of a little copper in the nickel, crude nickel anodes may be used (*cf.*

<sup>1</sup> *The Min. Ind.*, 1903, p. 232.

<sup>2</sup> *Eng. and Min. Journ.*, 1897, vol. lxiii., p. 113. *Zeit. für Elektrochemie*, vol. iii. p. 519.

such crude nickel containing 95 per cent. of the metal as is prepared at the Orford works). If insoluble anodes like carbon be employed the electrolyte, at first neutral, becomes acid in time, and conversely, when soluble anodes like crude nickel are used, it becomes alkaline. Fontaine therefore proposes to employ anodes of both crude nickel and carbon together in the same bath, so that by their combined action the electrolyte may be kept neutral.

The anode slimes containing the precious metals are treated by boiling them with dilute sulphuric acid to remove impurities, and by melting the residues, and casting them into anode plates and electrolysing them by the Moebius process (Vol. I., p. 913). In this way silver is deposited at the cathode, whilst gold and platinum collect in the anode slimes. The latter are dissolved by treatment with aqua regia, and the silver present in them is converted into insoluble chloride. From the solution gold is precipitated with ferrous sulphate, and the platinum is isolated as the ammonium platinum-chloride.

This process is said to have been tried experimentally at the works of the Canadian Copper Co., Cleveland, Ohio, though nothing is known of the result obtained. It is possible that the process has been supplanted by the electrolysis of copper-nickel alloys obtained from Canadian ores, which is said to be worked on a large scale at present in North America.

Browne's process<sup>1</sup> for the treatment of these alloys is said to be in use at Cleveland, Ohio.<sup>2</sup> The alloys are cast into anode plates; the cathodes are at first (while copper is being deposited) copper plates, and the electrolyte is a solution of the chlorides of copper and nickel. The impoverishment of the electrolyte during the deposition of the copper is made good by causing it to flow continuously through a tower, where it comes in contact with nickel-copper matte or alloy, sodium chloride solution and chlorine, the chlorine being generated during the electrolysis of the nickel chloride solution. During the first part of the electrolysis copper is deposited at the cathode and the nickel remains in solution. When the concentration of the latter has reached a certain point, the liquor is run off, the residual copper precipitated with sulphuretted hydrogen, the iron removed (though in what way is not stated) and the purified liquor then electrolysed between carbon anodes and sheet-nickel cathodes. Nickel is deposited at the cathodes, and the chlorine evolved at the anodes is led, as stated above, into a tower containing

<sup>1</sup> Canadian Pat., January 14, 1902, No. 74401.

<sup>2</sup> *The Min. Ind.*, 1902, p. 497.

nickel-copper matte and alloy. The arrangement for collecting and leading off the chlorine is shown in Fig. 484. *D* are closed spaces over the anode *A*, the electrolyte in the bath *C* acting as a water-seal. *B* are the cathodes, *F* is the outlet pipe for the chlorine, and *E* a pipe for leading in ammonia to the bath. Further details on the method and results and the apparatus used are lacking.

Ulke<sup>1</sup> uses as anodes copper-nickel alloys containing not more than 20 per cent. of nickel and not less than 80 per cent. of copper. The cathodes during the deposition of copper are made of sheet copper, and the electrolyte during the same interval is a hot solution of nickel and copper sulphate, acidified with sulphuric acid. As the copper is rapidly withdrawn from this during the process, small

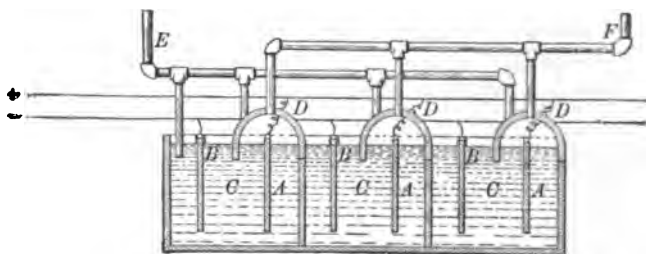


FIG. 484.

quantities of the liquor are frequently run off from the bath and replaced by fresh solution. The liquor thus run off is deprived of this copper by precipitation with hydrogen sulphide, and the precipitate of copper sulphide is said to be dissolved in hot sulphuric acid, the hydrogen sulphide formed in this reaction being used to precipitate copper from impoverished liquor, and the copper sulphate solution to replace partly the liquor run off from the bath.

The nickel sulphate solution thus freed from copper is made ammoniacal and electrolysed hot between anodes of sheet lead and cathodes of sheet nickel. To prevent undue exhaustion of the nickel, certain quantities of the electrolyte are run off periodically and replaced by fresh liquor. The partially spent liquor is treated for ammonia and nickel sulphate, both of which are employed again in the process.

By the withdrawal from time to time of part of the electrolyte, and its replacement by fresh liquor, the electrolyte is kept at the requisite strength for the deposition of copper and nickel respectively so that the process is a continuous one. Details are wanting, but

<sup>1</sup> *The Min. Ind.*, 1902, p. 497.

the process is said to yield nickel of good quality, and factory from the economic point of view.

The process now to be described is said to be used Superior Co.<sup>1</sup> Anodes, containing 90 per cent. of copper per cent. of nickel, along with a few ounces per ton of platinum, and palladium, are prepared by working Canadian nickel-copper matte with copper matte or copper concentrates. These anodes are subjected to treatment in the same way as are the coarse-copper in refining of copper, the only difference being that the electrolyte are withdrawn at intervals and replaced by copper sulphate, so that too great a concentration of electrolyte is prevented. The liquor thus withdrawn contains copper and iron (though in what way it is not stated), nickel sulphate, and this converted into a mixture of nickel of nickel. The mixture of these, contained in a basket the anode in a circuit, the electrolyte being a hot solution of sulphate. The application of soluble anodes is said to give better results than electrolysis of nickel sulphates with insoluble

Electrolytic refining of crude nickel obtained from Canada was for some time carried out successfully by the Balmain and Refining Co., Newark, near New York.<sup>2</sup> The process was kept secret, was begun in 1894, but was stopped when the works which supplied the crude nickel undertook the refining themselves. According to Ulke<sup>3</sup> the process was in operation in 1900, and 1,000 tons of electrolytic nickel were produced. The electrolyte was hot nickel sulphate. For 1 h.p. of energy, i.e., on the average 15 ampères per square foot at 2 to 4 volts, 2 to 4 tons of nickel were produced per year. The anodes contained 94 to 97 per cent. of the metal; the refined nickel did not contain over 0.25 per cent. of iron. The reason back to the process is said to have been the large quantities of gas formed by the ready disintegration of the imperfectly cast brittle anodes. This could be partly got over by using cast anodes, framework anodes containing the nickel in a metallic or imperfectly reduced granulations, or of powdered nickel or by connecting the crude-nickel plates in series so that the gas deposited on the cathode sides protected the anode sides from disintegration.

<sup>1</sup> *The Min. Ind.*, 1903, p. 491.

<sup>2</sup> *Eng. and Min. Journ.*, 1897, lxiii. p. 113. *Zeit. für Elektrochemie*, 1897, p. 519.

<sup>3</sup> *Electrochemical Industry*, 1903, vol. i., p. 208.

The crude nickel prepared at the Orford Works, Constable Hook, N.J., contained :—

Ni	. . . . .	95 to 96 per cent.
Cu	. . . . .	0.2 to 0.6 per cent.
Fe	. . . . .	0.75       "
Si	. . . . .	0.25       "
C	. . . . .	0.45       "
S	. . . . .	3.00       "

The sulphur was added intentionally to facilitate the casting of the metal into anode plates. The nickel deposited at the cathode contained :—

Ni	. . . . .	99.5 to 99.7 per cent.
Cu	. . . . .	0.1 to 0.2       "
Fe	. . . . .	0.1               "
S	. . . . .	0.02             "
As	. . . . .	0.03             "
Pt	. . . . .	trace

#### IV. REFINING OF COARSE NICKEL.

Although formerly coarse nickel contained only 60 to 90 per cent. of pure nickel, at the present time a metal can be obtained from the most diverse ores with 98 to 99 per cent. of pure nickel, and containing only very small quantities of impurities—cobalt, copper, iron, zinc, sulphur, arsenic, silicon, carbon, magnesium.

The composition of some of the earlier samples of coarse nickel is shown by the following analyses :—

	Joachimsthal. Per cent.	Klefva. Per cent.	Schladming. Per cent.
Ni . . . . .	86.5—71.4	83.0—90	86.7—88
Cu . . . . .	trace—18.9	1.3—0.2	1.8—1.9
Fe . . . . .	0.2—1.3	0.2—0.4	1.8—1.9
Co . . . . .	0.9—12.0	5.5—11.2	6.8—7.4
As . . . . .	0.0—0.6	—	0.7—0.8
Na . . . . .	—	9.9—0.2	—
S . . . . .	trace—0.1	0.7—1.4	—
SiO <sub>2</sub> . . . . .	0.0—3.5	0.7—0.9	0.0—1.0
Residue . . . . .	0.6—1.6	—	0.0—0.8

Two of the later samples of coarse nickel are composed as follows :—

	Iserlohn. Per cent.	New Caledonia. Per cent.
Ni . . . . .	99.6	0.98
Cu . . . . .	0.2	
Fe . . . . .	0.2	
C . . . . .	0.3	0.13
Si . . . . .	—	0.50
Mn . . . . .	—	1.53



Crude nickel is refined either electrolytically or in the former method has already been described. The removal of some of the impurities is attempted in the refining of coarse nickel, by obtaining a nickel monoxide as pure as possible. The removal of impurities at a later stage by an oxide is of the coarse nickel is only possible when they are more easily acted on by the oxygen of the air than nickel is (such as silicon, carbon, and iron). Thus the processes of Wharton in 1854 and of von Bischoff in Pfannenstiel, aim at removing silicon by a sort of puddling process. At the metal factory of Berndorf near Vienna, carbon is removed from the cubes of nickel, reduced at a moderate heat, in a 4 per cent solution of alkaline manganate or permanganate,<sup>1</sup> and then fused at a high temperature. A metal capable of being hammered is thus obtained. Garnier<sup>2</sup> removed iron from coarse nickel by fusing large quantities of it—such as is obtained by the direct reduction of garnierite—by fusion in a Siemens furnace with quartz. He has also suggested a reverberatory furnace with a bed of powdered limestone.<sup>3</sup> In this method carbon dioxide is evolved and serves as an agitator, and sulphur is said to be removed from the nickel by the excess of lime and carbon. The working of the New Caledonian ores into a matte, the processes of which seem hardly to have passed the experimental stage, have fallen into disuse.

At present the object always is to work up coarse nickel, obtained by the processes described, into a compact malleable metal. Pure nickel oxide is worked so as to give the same result. The method consists in fusing the metal with lime, and removing from the molten mass, by selected fluxes, silicon, oxide, carbon monoxide, and nickel cyanide.

Nickel monoxide dissolves in molten nickel just as cuprous oxides in their corresponding metals. It makes the metal brittle.

Carbon monoxide is readily absorbed by molten nickel, and makes the metal spongy.

Cyanide of nickel, which, according to Fleitmann, is not absorbed in the molten metal, makes it brittle.

Of the methods described below for the removal of the

<sup>1</sup> Ger. Pat., No. 28989.

<sup>2</sup> *Berg- und Hüttenm. Ztg.*, 1878, p. 245 ; 1879, p. 15.

<sup>3</sup> *Stahl und Eisen*, 1883, p. 518.

impurities, the one suggested by Fleitmann of adding magnesium has proved the most effective.

By the addition of magnesium to the molten metal, nickel monoxide and carbon monoxide are reduced to nickel and carbon respectively. Nickel cyanide is decomposed, nickel being set free and volatile magnesium cyanide formed.

To refine the nickel it is fused in crucibles of graphite, lined with burnt fire-clay; these hold between 33 and 90 lbs. of nickel. The same sort of crucible is used for the production of pure nickel from pure nickel oxide. The graphite crucibles used in the Orford Works are 18 inches high and 14 inches wide at the top and hold about 80 lbs. of monoxide with 16 per cent. of coal for reduction.

It is not advisable to add fluxes in fusing nickel, for they attack the crucibles strongly.

At the Westphalian Works<sup>1</sup> the crucibles, when filled with coarse nickel, are first heated in a wind furnace with coke fuel, and then placed in a furnace built on the Sefström principle, urged by an air-blast. Each of these latter furnaces takes only one crucible.

After the nickel is melted, which is said to take about an hour and a half, a small quantity of magnesium is added, and the metal poured. The magnesium is kept immersed by the help of a bar of pure nickel or fire-clay.

Fleitmann, the discoverer of the purifying action of magnesium, added at first  $\frac{1}{8}$  per cent. of magnesium to produce ductile castings,<sup>2</sup> but afterwards he diminished this quantity by using magnesium alloys instead of magnesium, especially the alloy with nickel. When zinc is present in the metal to be purified, to the extent of 4 or 5 per cent., the least addition of magnesium is necessary. Such nickel may be formed by the reduction of the oxides of zinc and nickel intimately mixed. With this  $\frac{1}{20}$  per cent. of magnesium is enough: it makes the metal very ductile, and also gives it the power of being welded to itself, or to iron and steel. In consequence of this property it can be made into nickel plated sheets 0.004 inch thick.

The quantity of magnesium can be still further reduced if reducing gases, such as hydrocarbons, hydrogen, or carbon monoxide, are first blown through the molten metal.

In the following analyses by Knorre and Pufahl may be seen the composition of three kinds of nickel before and after the addition of magnesium. These were melted at the works of Basse and Selve in

<sup>1</sup> *Oesterr. Zeitschrift*, 1894, p. 326.

<sup>2</sup> Ger. Pats., Nos. 6365, 7569, 9405, 13304, 14172, 23500, 28460, 28924.

Altena, in graphite crucibles lined with fire-clay, each containing about 70 lbs. About  $1\frac{1}{2}$  oz. of magnesium was added to each pot; the nickel obtained could be forged.

## COMPOSITION OF ORIGINAL SAMPLES.

	I.	II.	III.
Nickel . . . . .	97.87	97.90	98.21
Cobalt . . . . .	1.45	1.25	1.19
Iron . . . . .	0.45	0.50	0.25
Copper . . . . .	0.10	0.07	0.07
Silicon . . . . .	0.19	—	—
Silica . . . . .	—	0.19	0.24
Carbon . . . . .	trace	trace	trace
Sulphur . . . . .	0.05	—	trace
	100.11	89.91	99.86

## COMPOSITION AFTER ADDITION OF MAGNESIUM.

	I.	II.	III.
Nickel . . . . .	98.24	97.76	98.38
Cobalt . . . . .	1.09	1.33	1.04
Iron . . . . .	0.36	0.60	0.32
Copper . . . . .	0.10	0.09	0.07
Silicon . . . . .	0.06	0.10	0.07
Magnesium . . . . .	0.11	0.11	0.12
	99.96	99.90	100.00

Instead of magnesium there are other substances that can be employed to remove the same injurious impurities in nickel, but all seem to have been entirely surpassed by magnesium. Amongst these are black flux and coal, aluminium, calcium, calcium-zinc, manganese, phosphorus, potassium ferrocyanide, and ferrous cyanide.

At the Berndorf Works, black flux and coal were used at one time. The vapour of potassium seems to be set free and to act as a reducing agent.

Aluminium appears to be less active than magnesium. Calcium and calcium-zinc should act energetically, but are more expensive than magnesium.

Manganese, suggested as a purifier by Garnier in 1876, seems to have given good results at the works of H. Wiggin and Co., in Birmingham, where it was added in quantities of  $1\frac{1}{2}$  to 3 parts to 100 of the metal before casting; an addition of more than 5 per cent. is said to make nickel hard. Manganese peroxide can also be mixed with the nickel oxide before reducing. At the Basse and Selve Works about  $2\frac{1}{2}$  to 3 per cent. of the peroxide is said to be added to the nickel oxide before it is made into cubes.<sup>1</sup> Thus manganese peroxide is reduced to metal in the subsequent reduction. The metal combines with oxygen and will be separated in the slag.

<sup>1</sup> Ger. Pat., No. 25798.

Fleitmann<sup>1</sup> uses manganese to separate sulphur from nickel. Coarse nickel or the monoxide is melted with charcoal in a cupola furnace and then the liquid metal run into a Bessemer converter. To this is added manganese or a manganese alloy, by which the sulphur is carried into a slag. After this has been removed from the surface of the molten mass, air is blown through to oxidise carbon, manganese and iron. After the carbon has burned out, a mixture of air and oxygen, or oxygen alone, is blown in, so as to increase the temperature of the whole and ensure the complete combustion of the iron. Finally the excess of oxygen now present in the liquid metal is said to be removed by a fresh addition of manganese-nickel, or by powdered charcoal, or by gaseous reducing agents, carbon monoxide, a hydrocarbon or hydrogen.

Nickel obtained by these means is said to be very good for rolling and hammering.

Phosphorus was tried as early as 1855 by Ruolz and Fontenay. It has the power of combining with more oxygen, weight for weight, than any of the other agents. It has also, according to Garnier, the property of increasing the hardness of nickel at the expense of its malleability, if more than the three-thousandth part is present. Garnier, therefore, has adopted a phosphor-nickel with about 6 per cent. phosphorus. He prepares this alloy by fusing a mixture of nickel, carbon, calcium phosphate, and silica.

According to Manhes,<sup>2</sup> sulphur is removed from coarse nickel by smelting it in a regenerative reverberatory furnace, with a mixture of lime and calcium chloride or chloride of lime, on a hearth with a basic lining. This mixture must be laid in a fairly deep layer on the hearth, and on top of it the metal to be refined, in granulated form, and mixed with lime and the chloride of calcium or chloride of lime. At a sufficiently high temperature part of the sulphur passes off as dioxide and the rest goes into the slag, as basic sulphide.

According to Wedding the addition of magnesium is necessary for a compact forgeable metal.

Compact metal may be also obtained if the monoxide is mixed with powdered charcoal, heated to the reduction point in graphite crucibles, and then fused.

Molten nickel is poured into cast-iron moulds. If it is to be used in making alloys, it is granulated by pouring it into water.

<sup>1</sup> Ger. Pat., No. 73243, July 20, 1892.

<sup>2</sup> Ger. Pat., No. 77427, January 21, 1894.

# COBALT

## PHYSICAL PROPERTIES

Cobalt possesses a reddish-grey colour and considerable lustre: it is ductile at a red-heat, but at ordinary temperatures it is hard and brittle, and is suitable for the manufacture of cutting tools, on account of its hardness. It has a granular fracture. Its specific gravity is said to be between 8·5 and 8·9; that of the metal reduced by hydrogen is 8·957, according to Rammelsberg. It is magnetic, melts between 1600° and 2000° C., and cannot be volatilised. Regnault gives the specific heat as 0·10696.

## THE CHEMICAL PROPERTIES OF COBALT AND OF ITS MOST IMPORTANT COMPOUNDS

Massive cobalt does not change in either damp or dry air, but the metal which has been reduced in hydrogen at the lowest possible temperature, or that which has been prepared at a low temperature from the oxalate, is pyrophoric. On heating cobalt in oxygen it burns with a red light forming the oxide: at a red heat it decomposes water.

It dissolves slowly in hydrochloric and sulphuric acids with liberation of hydrogen, and easily in hot dilute nitric acid, forming in each case a solution of the corresponding cobaltous salt. It absorbs carbon when heated with it; combines directly with sulphur, the halogens, phosphorus, arsenic, antimony and silicon; it can be precipitated by the electric current from its solutions, and in other respects resembles nickel very closely in its properties.

## OXIDES

It forms three oxides:—Cobaltous oxide,  $\text{CoO}$ , cobaltoso-cobaltic oxide,  $\text{Co}_3\text{O}_4$ , and cobaltic oxide,  $\text{Co}_2\text{O}_3$ , all of which are black, and can

be reduced to metal by carbon or hydrogen at a high temperature. Cobaltic oxide combines with water to form a dark-brown powder, the hydrate  $\text{Co}(\text{OH})_3$ , which when heated passes successively into  $\text{Co}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{CoO}$ . The principal salts of cobalt are those derived from cobaltous oxide.

#### COBALTOUS SULPHIDE, $\text{CoS}$ ,

is obtained as a blackish-brown precipitate when aqueous solutions of cobaltous salts are treated with an alkaline sulphide. This precipitate is insoluble in dilute hydrochloric acid. When heated by an electric current it behaves similarly to nickel sulphide.

#### COBALTOUS SULPHATE, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ,

forms a soluble double salt with ammonium sulphate which, like the corresponding nickel salt, serves for the electrolytic deposition of the metal.

Potassium nitrite when added to solutions of cobaltous salts precipitates *potassium-cobalti-nitrite*,  $\text{KNOCo}_2(\text{NO}_2)_6$ ; as a yellow crystalline powder.

The so-called *cobaltamines* are compounds of cobaltic chloride with varying amounts of ammonia, and are formed by the oxidation of ammoniacal solutions of cobaltous chloride. Roseocobaltous chloride,  $\text{Co}_2\text{Cl}_6 \cdot 10\text{NH}_3 + 2\text{H}_2\text{O}$ ; Purpureo-cobaltous chloride,  $\text{Co}_2\text{Cl}_6 \cdot 10\text{NH}_3$ ; Luteocobaltous chloride,  $\text{Co}_2\text{Cl}_6 \cdot 12\text{NH}_3$  are some of these bodies. When heated, they are all converted into pure metallic cobalt, and have been proposed for its manufacture.

#### COBALT ORES

The ores of cobalt which serve for the production of the oxide or *smalt* are *speiss-cobalt*, *cobaltine*, *cobalt-pyrites* and *earthy cobalt*. The other minerals in which cobalt occurs possess a mineralogical rather than a metallurgical interest.

*Speiss-cobalt*, *smaltine*, or *tin white cobalt*,  $\text{CoAs}_2$ , which, when pure, contains 28.2 per cent. of cobalt, occurs in Saxony at Freiberg. Schneeberg and Annaberg; in Prussia at Riechelsdorf; in Bohemia at Joachimsthal; in Hungary at Dobschau; at Tunaberg in Sweden; at Allemont in France; in Cornwall, and in the State of Missouri. U.S.A.

*Cobaltine*, *bright white cobalt* or *cobalt glance*,  $\text{CoAsS}$ , contains when pure 35.5 per cent. of cobalt, but usually a portion of the cobalt is replaced by nickel and iron. It is found at the following

places :—In Sweden at Tunaberg, Riddar-hyttan, Gladhammar and Vena near Annaberg; in Norway at Skutterud; in England at Botallack, Cornwall; in Germany at Querbach (Silesia), and Siegen (Westphalia); in Russia at Daschkesan (Caucasus); at the latter place it occurs in felsite porphyry and is free from nickel.

*Earthy cobalt, asbolan* or *uad*, is a mixture of varying quantities of cobaltous oxide, with manganese peroxide, and ferric hydrate. The proportion of cobalt varies from 2 to 20 per cent. It occurs in small quantities on the outcrop of cobalt ore deposits. Extensive deposits of it have been discovered in New Caledonia, and contain from 3 to 5 per cent. of cobalt. Similar deposits have been found at Port Macquarie, N.S. Wales.<sup>1</sup> It also occurs at Asturias in Spain, and there contains 15 per cent. of the metal.

Other cobalt minerals which deserve mention, although, on account of their comparative rarity, they do not form the basis for a separate process of extraction, are :—*Linnæite*,  $\text{Co}_3\text{S}_4$ , which often contains more nickel than cobalt and is then known by the name *cobalt nickel pyrites*; it occurs in Sweden; at Müssen near Siegen; at the Motte mine in the State of Missouri :—*cobalt bloom* or *erythrine*,  $\text{Co}_3\text{As}_2\text{O}_8 + 8\text{H}_2\text{O}$ , which occurs in the outcrop of cobalt ore deposits, usually those of arsenical ores; it is found at Schneeberg, Saalfeld, Riechelsdorf, Siegen, Cornwall and Cumberland :—*cobalt vitriol* or *bieberite*,  $\text{CoSO}_4 + 7\text{H}_2\text{O}$ , which occurs at Bieber in Hesse. Cobalt ores are nearly always found with nickel ores; the metal is found with nickel and iron in meteorites.

#### METALLURGICAL PRODUCTS CONTAINING COBALT WHICH ARE USED AS SOURCES OF SMALT AND COBALT MATTE

These are matte, speiss and slag. The cobalt which exists in small quantities in a great variety of ores, especially in those of nickel, is collected into speiss or matte, and may be extracted from these even when present in very small quantity. Cobalt is also found in slags produced from matte containing cobalt and nickel, when these are treated by oxidising fusion.

#### THE EXTRACTION OF COBALT AND COBALT COMPOUNDS

Metallic cobalt has had a very limited technical application up to the present time, and is produced only in small quantities and by methods exactly similar to those in use for the production of nickel, viz., by the reduction of cobaltous oxide,  $\text{CoO}$ , or cobaltic

<sup>1</sup> *The Min. Ind.*, 1902, p. 492.

oxide,  $\text{Co}_2\text{O}_3$ . Cobalt ores, however, are used in very large quantities for the production of *smalt*, a silicate of cobaltous oxide and alkalis, which possesses an intense blue colour, and is used as a pigment. (Silicate of cobalt itself is an exceedingly strong colouring agent, surpassed only by gold. A proportion of one-tenth per cent. in glass gives it a deep blue colour.) Other cobalt pigments are produced in smaller quantities; such are the phosphate, the arseniate (known as *red oxide of cobalt*), *cobalt bronze*, which is a double phosphate of cobalt and ammonium, *cobalt ultramarine* or *Thenard's blue*, which is an intimate molecular mixture of alumina with different oxides of cobalt, *Rinmann's green*, and others.

Up to the present time metallic cobalt has been prepared only by wet methods. The metal is precipitated from solution as the sesquioxide  $\text{Co}_2\text{O}_3$ , which is afterwards reduced by charcoal. The production of the metal entirely by dry methods has not yet proved practicable on account of the impurities of the ores or metallurgical products employed. Many methods have been proposed to prepare it electrolytically, but none of these seem to have had industrial application, although electrolytic coatings of the metal have been obtained on other metals and alloys. All that has been said before about the electro-metallurgy of nickel applies equally to cobalt.

For the reasons given above the extraction of cobalt is more frequently carried on in chemical works than in smelting houses, and the methods employed are largely kept secret, as in the case of nickel.

A dry direct process for the treatment of rich cobalt ores is used for the production of *smalt*, and also to a smaller extent for the preparation of cobalt arseniate. Other cobalt compounds are prepared in chemical works from cobaltic oxide or from salts of cobalt by means of wet methods.

We therefore have to distinguish :—

- (1) The extraction of cobalt oxide,  $\text{Co}_2\text{O}_3$ , and metallic cobalt.
- (2) The production of *smalt*.

## 1. THE EXTRACTION OF COBALT OXIDE AND METALLIC COBALT

Cobalt oxide is the starting point in the preparation of the pure metal and of its various compounds.

### A. THE EXTRACTION OF COBALT OXIDE

Pure cobalt oxide in quantity has as yet been prepared only by wet methods, either from ores or from furnace products. The oxide



resulting from roasting ore, speiss or matte which contains sulphur or arsenic, or both, is always too impure, and requires to be dissolved in order to remove impurities and to obtain a pure product. It has been proposed<sup>1</sup> to produce from sulphuretted ores a matte free from iron, and containing only sulphur and nickel besides the cobalt: this matte was to be fused under a blast on a bed of quartz and sodium silicate in order to produce a silicate of cobalt, and this latter was to be fused with soda and nitre in order to liberate the cobalt oxide. The method, however, does not appear to have come into use.

The common methods for producing cobalt oxide from ores which but rarely contain any ingredients beside nickel, iron and (principally) copper, in addition to the cobalt, has already been described under nickel, for the wet methods for the extraction of nickel are usually preceded by a separation of cobalt in the form of sesquioxide. These will accordingly be found under nickel.

The compounds containing sulphur, arsenic, sulpharsenides, &c., are first dead roasted in order to drive off sulphur and arsenic and convert the heavy metals into oxides. The same object may be attained by the more costly method of smelting the unroasted ore with soda and saltpetre, or with sulphur and soda-ash, or potash; in this case arseniates and sulpharseniates, or sulphates of the alkali are formed, and may be removed by lixiviation, the heavy oxides being left behind.

The oxides so obtained, or the ores where these already contain the metals as oxide, are treated with hydrochloric or sulphuric acids, which dissolve the cobalt, nickel, iron, copper, and other soluble oxides. Lead, copper and bismuth are precipitated from the solution thus obtained by sulphuretted hydrogen or an alkaline sulphide, and the solution, when separated from the precipitated sulphides, is treated with the exact quantity of chloride of lime necessary to convert the ferrous into ferric oxide, which latter is then thrown down by the addition of powdered chalk.

(The bismuth could be thrown down from the hydrochloric acid solution by the addition of water, in the form of basic chloride, instead of being precipitated with the lead, copper, &c., by means of sulphuretted hydrogen.)

The cobalt is precipitated from the liquid, after the iron has been removed, by the cautious addition of chloride of lime to the warmed solution. It is thrown down as sesquioxide, and unless care is taken to avoid excess some nickel comes down with it. The

<sup>1</sup> Muspratt-Kerl, *Handb. der Techn. Chem.*, 3rd ed., vol. iii., p. 1938. *Graham-Otto, Chemistry*, 1889, p. 915.

solution which remains after the cobalt has been separated yields nickel when treated as before described. Cobalt may also be precipitated after the nickel. In this case soda is added to the boiling solution, which precipitates nickel monoxide with a small amount of cobalt monoxide, while cobalt with a trifling quantity of nickel remains dissolved. It may now be precipitated as sesquioxide by adding more soda, or by chloride of lime.

Another method for the separation of cobalt and nickel consists in first neutralising the concentrated solution with potash lye, then making it faintly acid with acetic acid, and treating it with potassium nitrite, which throws down cobalt as potassium-cobalti-nitrite, nickel remaining in solution. When the precipitate is ignited it is converted into cobalt sesquioxide. If lime is present, potassium nitrite is of no use for separation, for Erdmann finds that in that case a salt of nickel and calcium is also precipitated ( $K_2CaNi(NO_2)_6$ ). Other alkali salts have also been proposed for the purpose.

Patera formerly employed bisulphate of potash, which throws down nickel completely as a difficultly soluble double salt containing a small quantity of the cobalt compound.

According to Kunzel, bisulphate of ammonia is more suitable. The latter precipitates the nickel double salt when the solution is sufficiently concentrated, while the cobalt compound remains in solution. From this solution cobalt is precipitated as sulphide by ammonium sulphide, and this is converted into sesquioxide by roasting.

As instances of the recovery of the sesquioxide from smelting products containing nickel and cobalt, we may take the process at the Scopello Works, already described under nickel (p. 725), and at the George Works at Dobschau (p. 729); and also the method at the Editha Smalt Works in Silesia, and at similar works at Oberschlema in Saxony.

Lundborg<sup>1</sup> describes the treatment at the Editha Smalt Works of ores containing earthy cobalt, with concentrated hydrochloric acid in clay vessels, steam being blown through. Iron is first thrown down from the solution by adding separate small portions of marble and keeping at a certain temperature. As soon as nickel begins to come down, the separation of iron is known to be complete.

Soda is now added to the filtrate to precipitate nickel. When cobalt begins to come down, the liquid is filtered, and precipitation continued, a mixture of the two monoxides now falling until all the nickel has separated. Lastly, pure cobalt monoxide may be thrown down from the final filtrate. The precipitate of mixed oxides is

<sup>1</sup> *Jern. Cont. Annalen*, 1876, pt. 2; *Berg- und Hütt. Ztg.*, 1877, p. 35.

accumulated and redissolved, and the two separated similarly by fractional precipitation.

The matte from the Sesia Works at Oberschlema, in Saxony, is similarly treated. It contains 16 per cent. Ni, 14 per cent. Co, 50 per cent. Cu, and 20 per cent. S. The powdered matte is roasted in a reverberatory furnace and treated with dilute sulphuric acid. The copper is first precipitated by iron, after which the remainder of the process is the same as that described above. Extraction of cobalt from roasted ores and smelting products, or from oxidised ores, by means of mineral acids, may be carried on if there are not many other substances present which will dissolve in the acid; it is especially important that the ores do not contain too much soluble gangue; otherwise, with a rather poor material originally, the successive filtrates will be so impure and contain so little cobalt that it will be barely, or not at all, worth while to work them up into the sesquioxide. For the working of such mixtures methods have been proposed by Herrenschmidt and Stahl, which will now be shortly described.

Herrenschmidt's<sup>1</sup> method, already described under wet methods for nickel, is used at the Malétra Co.'s works at Petit Querilly, near Rouen; it has for its object the working up of oxidised cobalt ores, and especially one from New Caledonia, an *asbolan*, containing nickel, manganese, and iron, mingled with clay. The average composition of this ore is:—<sup>2</sup>

MnO . . . . .	18	per cent.
CoO . . . . .	3	"
NiO . . . . .	1·25	"
SiO <sub>2</sub> . . . . .	8	"
Fe <sub>2</sub> O <sub>3</sub> . . . . .	30	"
Al <sub>2</sub> O <sub>3</sub> . . . . .	5	"
CaO . . . . .	1	"
MgO . . . . .	1	"
Loss by ignition . . . . .	32·75	"

The finely powdered ore is treated with ferrous sulphate solution, which deposits ferric oxide and brings cobalt, nickel, and manganese into solution as sulphates. To facilitate solution the whole is agitated by a current of steam. (The green vitriol solution is made in the works by acting on cuttings of iron with sodium bisulphate solution and separating ferrous from sodium sulphate by crystallisation.)

<sup>1</sup> *Genie civil*, 1891, 18, 373; *Monit. Scientif.* vol. vi., May, 1892; *Berg- und Hüttenm. Ztg.*, 1892, p. 464; 1893, p. 1. <sup>2</sup> *Berg- und Hüttenm. Ztg.*, 1892, p. 464.

The solution containing the three sulphates is separated from the residue by a filter press, and treated with sodium sulphide in precipitation vats, whereby the whole of the cobalt and nickel and a small portion of the manganese are precipitated.

(The sodium sulphide is made in the works by treating the black residues of the Leblanc soda process with sodium sulphate and water and warming, when by double decomposition calcium sulphate is separated and a solution of sodium sulphide is obtained.)

The precipitate of metallic sulphides is separated by a filter press, and treated with solution of ferric chloride, which decomposes and dissolves manganese sulphide but does not act on the other two. A fairly pure residue of nickel and cobalt sulphides is thus obtained, and a liquid containing manganese sulphate and manganese chloride with ferric and ferrous sulphates and chlorides. This liquid after being separated may be treated with excess of chalk, and air blown through, which gives a precipitate of calcium manganite, that can be worked up with the Weldon mud in the manufacture of chlorine.

The two sulphides thus freed from manganese are dried and subjected to a careful roasting to convert them into sulphates. The latter are washed out by hot water, and treated with calcium chloride which forms their soluble chlorides, precipitating calcium sulphate. The filtered liquid has to be freed from the small amount of iron in it by copper oxide, and this copper thrown down by nickel monoxide. Then it is divided into two parts. From one cobalt and nickel are thrown down by lime as hydrates, the precipitate carefully washed and suspended in water, then treated with chlorine gas and air, which convert both hydrates into sesquioxides. The nickel sesquioxide so formed is now used to precipitate cobalt from the other half of the solution. For this purpose the precipitate of sesquioxides is added to the solution of the two chlorides and stirred about with the assistance of a current of steam. Nickel sesquioxide is reduced to monoxide and passes into solution, and the equivalent of cobalt sesquioxide is precipitated, with the original, which is not dissolved at all.

All the cobalt is now precipitated as sesquioxide, the nickel is dissolved as chloride. The latter may be thrown down from the liquid as monoxide by milk of lime.

The cobalt sesquioxide is washed, pressed, dried, and ignited.

When the nickel is precipitated the calcium chloride produced can be used in the process to act upon the sulphates (formed from sulphides by roasting).

Nothing is known yet as to the economic results of this method.

It seems to be most suitable to a Leblanc soda works, where chlorine is made by the Weldon process.

Stahl's<sup>1</sup> method consists in a chlorinating roasting of ores poor in cobalt with various chlorides and pyrites so as to form cobalt chloride; then the soluble salts are washed out of the product, cobalt precipitated from the liquid as sulphide, and this converted into oxide. Stahl discovered that a chlorinating roasting converted copper into nickel, cobalt, and chlorides almost completely, and manganese to a great extent, while iron is converted into oxide; (if the wash water is slightly acid it is impossible to prevent a little iron being dissolved). Any soluble alkali earths in the ores are converted into sulphates by the roasting. Calcium and magnesium sulphate pass into the solution with the chlorides of cobalt, nickel, copper, and manganese, and also freshly formed alkali sulphates and undecomposed alkali chlorides. (Calcium sulphate will be to a great extent thrown down by evaporating the wash liquor to a certain density.)

Stahl treats the liquor in the following way. First copper sulphide is thrown down by sulphuretted hydrogen, and filtered off. The liquid is neutralised by soda, and sodium sulphide added to precipitate sulphides of cobalt, nickel, iron, manganese and any copper remaining. Manganese is the last to come down, and so may be nearly all left in the solution by carefully regulating the amount of the precipitant.

To separate cobalt sulphide from the others, Stahl<sup>2</sup> treats them with a mixture of acetic and sulphurous acids until the solution is slightly acid. Sulphurous acid decomposes any sulphuretted hydrogen produced and prevents its being noxious. The residue is separated by a filter press, roasted to convert the sulphides into oxides, and then treated with hot pure soda lye to decompose any sulphates remaining; finally it is washed, dried, and ignited.

Stahl first tried this method on an ore of this composition:—

Co . . .	1.02 per cent.	Fe <sub>2</sub> O <sub>3</sub> . .	5.56 per cent.
Ni . . .	Trace	Al <sub>2</sub> O <sub>3</sub> }	1.06 "
As . . .	2.46 "	P <sub>2</sub> O <sub>5</sub> }	
Cu }	0.53 "	CaO }	0.81 "
Fe }		MgO }	
S }		Insoluble }	88.36 "
		residue }	

The ore was ground down to about 0.06 inch mesh, and placed in

<sup>1</sup> *Berg- und Hüttenm. Ztg.*, 1893, p. 2; Ger. Pat., No. 58417.

<sup>2</sup> Additional patent, No. 66265.

a long-bedded calciner; it was alternately oxidised and reduced during roasting to get rid of arsenic. Reducing was effected by adding sawdust. The product, free from arsenic, was subjected to chlorinating roasting in a special furnace (most likely a muffle furnace). For this purpose it was mixed with 15 per cent. of its weight of *Abraumsalz*<sup>1</sup> (which is 95 per cent. alkali chloride) and 10 per cent. of its weight of pyrites free from zinc and nickel; then it was roasted at a red heat until the cobalt was fully chlorinated. Stahl gives the following reactions:

1.  $8\text{FeS}_2 + 22\text{O}_2 = 4\text{Fe}_2\text{O}_3 + 16\text{SO}_2$ .
2.  $\left\{ \begin{array}{l} 12\text{NaCl} + 6\text{SO}_2 + 3\text{O}_2 + 6\text{H}_2\text{O} = 6\text{Na}_2\text{SO}_4 + 12\text{HCl}; \\ 2\text{Co}_3\text{O}_4 + 12\text{HCl} = 6\text{CoCl}_2 + 6\text{H}_2\text{O} + \text{O}_2 \end{array} \right.$
3.  $\text{Co}_3\text{O}_4 + 6\text{NaCl} + 3\text{SO}_2 + \text{O}_2 = 3\text{CoCl}_2 + 3\text{Na}_2\text{SO}_4$ .
4.  $\left\{ \begin{array}{l} 6\text{SO}_2 + 3\text{O}_2 = 6\text{SO}_3; \\ 2\text{Co}_3\text{O}_4 + 12\text{NaCl} + 6\text{SO}_3 = 6\text{CoCl}_2 + 6\text{Na}_2\text{SO}_4 + \text{O}_2; \end{array} \right.$

and so on.

The product was washed in lixiviating vats fitted with straw filters, four times with slightly acid water and then with pure water. This acid water was obtained by leading the gases from the roasting into condensation towers, where the acid portion was absorbed by water. The wash liquor contained 0.41 per cent. Co and Ni, 0.075 Cu, traces of iron and manganese, and small quantities of sodium chloride, calcium and magnesium sulphates, and appreciable quantities of alkali sulphates. The residue after washing contained 0.04 per cent. Co and Ni. Another ore containing 1.08 Co was similarly treated, and gave a liquor containing 0.429 per cent. Co, 0.006 per cent. Fe, 0.031 Mn, 0.004 Cu; and small quantities of salts just as above. The residue contained 0.07 per cent. Co.

Another ore of which the composition was:—

Co . . .	1.49 per cent.	$\text{Al}_2\text{O}_3$ }	2.52 per cent.
Ni . . .	0.02 "	$\text{P}_2\text{O}_5$ }	
As . . .	4.09 "	$\text{Mn}_2\text{O}_3$ . .	1.44 "
Cu }		$\text{CaO}$ }	0.36 "
Fe }	Trace	$\text{MgO}$ }	
S }		Alkali . .	Trace
$\text{FeS}_2$ . .	1.35 "	Insoluble }	74.96 "
$\text{Fe}_2\text{O}_3$ . .	14.02 "	residue }	

produced a liquor with 0.643 per cent. Co and Ni, 0.057 per cent. Fe.

<sup>1</sup> See vol. i., p. 11.

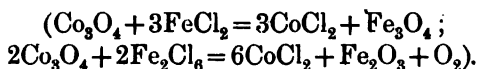
0.296 Mn. The residue contained 0.09 per cent. Co and Ni, 0.21 per cent. As, 21.10 per cent.  $\text{Fe}_2\text{O}_3$ , and 0.42 per cent.  $\text{Mn}_2\text{O}_3$ .

Ores with 2.81 per cent. Co, 0.04 per cent. Ni, and 7.29 per cent. As, were treated in the same way, and left residues with 0.11 per cent. Co and Ni, and 0.27 per cent. As.

By treatment of these liquors in the way described Stahl obtained an oxidised product with 92 per cent.  $\text{Co}_2\text{O}_3$ .

Whether this method was ever worked is not known to the author. It seems possible that, if the cost of reagents is low, poor ores containing about 1 per cent. cobalt can be worked by it with profit.

According to another method<sup>1</sup> the dead roasted ore is re-roasted with chlorides of iron, whereby cobalt chloride is formed with ferric oxide and ferroso-ferric oxide :—



As far as the writer knows, no experiments have been yet made on a large scale to ascertain whether the conversion of cobalt into chloride is complete.

Sack<sup>2</sup> has patented a process for separating cobalt from manganese, iron, and aluminium, based on his researches on lead peroxide and its hydrate. He found that when a liquid containing 0.308 per cent. Co and 0.4156 per cent. Mn was treated with lead peroxide at ordinary temperatures, the resulting liquid contained 0.3638 per cent. Co and 0.00076 per cent. Mn. The two metals were present as sulphates. Further he found that manganese peroxide would precipitate alumina. Iron, he showed, was thrown down as basic salt.

The liquid (preferably a solution of sulphates) is first freed from any copper it contains, and then well mixed with the calculated quantity of peroxide of lead. In case iron is present in great quantity it is precipitated beforehand by an alkali (or alkaline earth) carbonate, and a large proportion of manganese, if present, is got rid of by fractional precipitation with a soluble alkali or alkaline earthy sulphide.

The precipitate produced by lead peroxide, which consists of hydrated peroxide of manganese, alumina, basic ferric sulphate, and lead sulphate, is to be brought into solution (all but the lead) by

<sup>1</sup> Schoneis, *Berg- und Hüttenm. Ztg.*, 1890, p. 453; *Chemiker Ztg.*, 1890, p. 1475; *Zeitschr. angew. Chem.*, 1890, p. 337.

<sup>2</sup> Ger. Pat., Kl. 40, No. 72579, August 5, 1892.

sulphuric or hydrochloric acid, and the residue of lead sulphate worked up again into peroxide. This method does not appear to have been used on the large scale.

Vortmann<sup>1</sup> proposed to obtain cobaltic oxide or hydrate from solutions containing cobalt and nickel, by electrolysis. If a current is passed through solutions of these metals containing no alkali sulphates or other neutral salts of the alkalies, cobaltous and nickelous hydrates or basic salts of both come down at the cathode. If the current is reversed the nickelous hydrate (or corresponding basic salt) dissolves, but not that of cobalt, which is oxidised to cobaltic hydrate instead. On restoring the current to its original direction more of each lower hydrate is produced, and on again reversing the current the nickel is dissolved. In this way, finally, all the cobalt is precipitated as hydrate and all the nickel remains in solution. If there is a small quantity of a chloride present in the liquid (say 1 per cent. common salt), the cobaltous hydrate is very quickly oxidised to the higher compound by the small amount of free chlorine or hypochlorous acid set free. In this case the constant change of current is unnecessary.

The separation of cobalt is assisted by gentle warming. After it is completed, the current is stopped and the liquid heated to 60° or 70°, whereby any small quantity of nickelic hydrate remaining in the cobalt compound is dissolved away. The solution of nickel when filtered contains no cobalt. Vortmann's assumption that nickel and cobalt salts behave in this way on electrolysis does not always hold. The process has probably never come into use.

Coehn and Salomon's proposal<sup>2</sup> is to electrolyse mixed cobalt and nickel solutions so that peroxide of cobalt is deposited at the anode and nickel remains in solution, both nickel and cobalt being prevented from becoming deposited at the cathode by the addition of a copper salt to the electrolyte, the copper of which is precipitated on the cathode. It is not known whether this method has found application.

Another method<sup>3</sup> of theirs is to precipitate the cobalt by ammonium or some metallic persulphate, the latter being prepared electrolytically.

The metallic cobalt used by Winkler for atomic weight determinations was prepared by Bischoff and Tiemann as follows<sup>4</sup>:—The

<sup>1</sup> Ger. Pat., No. 78236, May 10, 1894.

<sup>2</sup> Ger. Pat., March 4, 1898, No. 102370.

<sup>3</sup> Ger. Pat., No. 110615.

<sup>4</sup> *Zeitschr. für. Inorg. Chemie*, vol. viii., 1895.



electrolyte consisted in the first seven experiments of 100 c.c. of a solution of cobalt sulphate (containing 1.164 per cent. of cobalt), 30 grams of ammonium sulphate, 30 grams of ammonium solution of density 0.905, and 100 c.c. of water. Both anodes and cathodes were of platinum foil. The tension was 3 volts, the current strength 0.7 ampère, and the current density  $D_{100}=0.6$  ampère. On heating the deposit in hydrogen it lost 0.23 per cent. in weight, and must thus have contained 0.32 per cent. of cobalt oxide. In later experiments the electrolyte was made up of 250 c.c. of the same solution of cobalt sulphate, 30 grams of ammonium sulphate, 50 grams of ammonium solution of the above density, and 250 c.c. of water. The anode was of platinum foil, the cathode of polished sheet nickel. The current strength was 0.8 ampère, the tension 3 volts, and the current density  $D_{100}=0.6$  ampère. On heating the deposited cobalt in hydrogen, it lost 0.15 per cent. and must thus have contained 0.21 per cent. of cobalt oxide. The metal after heating was of a bluish-white colour.

## B. THE EXTRACTION OF METALLIC COBALT

This is achieved by the reduction of the sesquioxide with carbonaceous bodies and is carried on exactly in the same way as the reduction of nickel from its monoxide.

The melted cobalt, free from carbon, can be cast into plates, which may be rolled when hot. The addition of a trace of magnesium (0.1 per cent.) assists the production of a compact and tenacious casting.

A patent <sup>1</sup> is in use at the Berndorf works in Lower Austria for the production of cobalt which is malleable and can be forged. The oxide is used in the form of powder; it is mixed with a 4 per cent. solution of alkaline permanganate, dried and smelted in a blast furnace, which gives cobalt containing a trace of manganese. The manganese compound renders the gaseous carbon compounds innocuous by oxidising them. A little is reduced and the manganese absorbed by the cobalt. (Carbon, which is taken up by cobalt to the extent of 4 per cent., makes it hard and brittle.)

## 2. THE PRODUCTION OF SMALT

Smalt is a potash glass highly silicated and coloured blue by cobalt monoxide. Various qualities, classified according to shade and fineness of grain, are found in commerce. It contains usually a

<sup>1</sup> Ger. Pat., No. 28989.

certain quantity of water-glass and also minute quantities of arsenic or arsenious acid. According to Ludwig<sup>1</sup> the colour may be injured in purity and strength by the presence of certain metallic oxides. According to his researches baryta deepens the colour somewhat, but gives it an indigo-blue tinge. Soda, lime, and magnesia diminish the colour in a marked degree, and give it a reddish shade. Alumina does not affect the purity of the colour, but diminishes its intensity. Nickel monoxide gives the glass a red colour if it is in small quantities; a large amount gives a violet-brown tint; ferrous oxide gives a shade varying from brown to green. Manganic oxide gives violet, cupric oxide green, cuprous oxide red shades. Ferric oxide, manganous oxide, lead and bismuth oxides are harmless if not in too great quantities. The quantity of cobalt in the smalt varies with its depth of colour from 1.95 to 18 per cent.

Smalt is manufactured by melting together in proper proportions cobaltic oxide, quartz, and potash.

The oxide is generally made direct from the ores by roasting, unless it is made by a wet method. If the ores to be roasted contain arsenical or sulph-arsenical compounds of cobalt, the roasting furnaces (reverberatory or muffle furnaces) must be provided with condensers to arrest the arsenious acid set free.

The roasting should be carried on so that the cobalt in the ore is converted into sesquioxide. If a considerable amount of iron or nickel is present, a certain amount of metallic arsenide is purposely left undecomposed to separate those metals in a speiss during the smelting process. But if the roasting is terminated too soon, cobalt will remain combined with arsenic, and pass into the speiss. A small quantity thus lost need not be regretted as it ensures the absence of nickel in the smalt. If iron is in the ore there is also advantage in keeping back a little arsenious acid in the roasted product, as during the smelting this will convert ferrous oxide into the much less injurious ferric oxide.

Silica is used in the form of pure ground quartz. To obtain this lumps of quartz are ignited, dropped into water so as to render them brittle, and then stamped. The pulverised quartz is finally washed to get rid of any foreign matter.

The potash must be pure and calcined, and must be free from soda and alkaline earths.

The ore, the quartz, and the potash are most intimately mixed in accurate proportions, either ascertained by experience or discovered by preliminary trials, and then put into the crucibles of the

<sup>1</sup> *Erdmann's Journ. pr. Chem.*, vol. li., p. 129.

smalt furnace. If there is not arsenious acid enough in the ore to oxidise the ferrous oxide, the requisite amount is added to the charge.

The smelting crucibles or pots are made of fire-clay, and vary in size in different works.

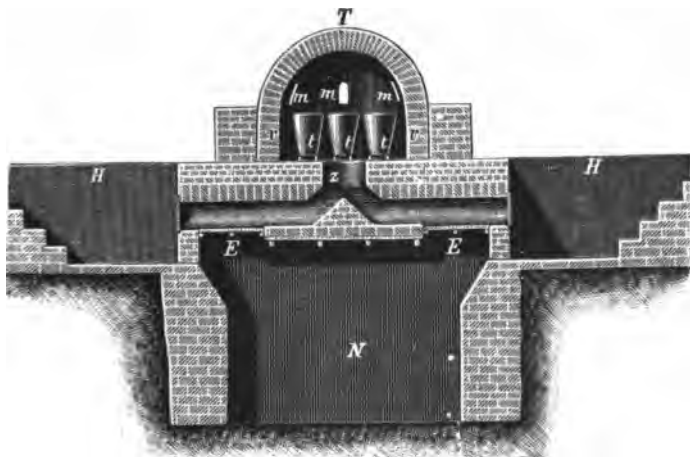


FIG. 485.

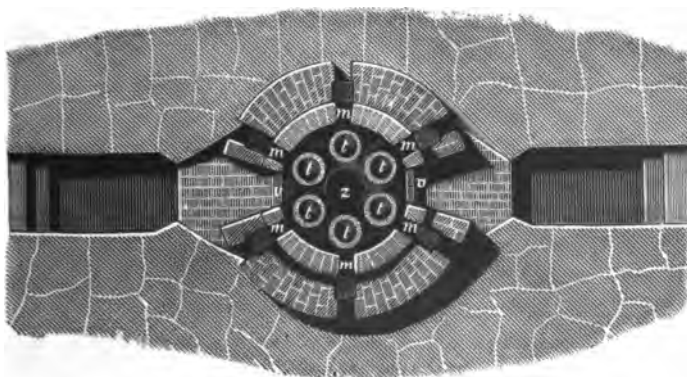


FIG. 486.

At the Saxony smalt works a pot holds about 1 cwt. of the mixture, and there are 8 pots in a furnace.

The arrangement of a furnace for 6 pots is shown in Figs 485 and 486.

On the bottom of the dome-shaped heating chamber *T*, the pots *t, t*, are placed on tiles round an opening *z*, through which the flame ascends from the two hearths *E, E*, below. The smoke and gases

after circulating round the pots, pass away through the openings *m, n*, which are also working doors. The pots are put in and taken out through the openings *v*, which are bricked up during heating. *N* is the ashpit, *H* the floor level of the works.

During the fusion cobalt sesquioxide, silica, and the potassium of the potash unite into a glass, the smalt, while nickel, iron, and copper unite with the arsenic into a speiss. Bismuth, if present, separates with the speiss. If copper is present as oxide, it yields its oxygen to the readily oxidisable metals, and is also found in the speiss.

The speiss and any bismuth present are found at the bottom of the pot, the cobalt glass above. While fusing, the mass is stirred up from time to time. Finally the molten mass is allowed to stand quiet for a while for the two layers to separate completely. Then the glass is lifted out with a ladle, and poured into cold water, to be ready for powdering.

The length of the operation varies from 8 to 16 hours according to the charge and the quality of the glass to be obtained.

On account of the purity of the speiss it is a suitable material for the recovery of nickel. If the ore contains bismuth, large quantities of this metal are mixed with the speiss. It is obtained by liquation before working up for nickel.

After being thrown into water, the glass is stamped, sieved, jigged to free it from any intermixed speiss, and then ground wet in mills. The mud is sent through a series of washing vats in which the glass powder is deposited according to the size of its granules. In the first is the coarse powder, called "*Strenblau*." This is ground again with glass of the same depth of colour. After this is removed, the mud is run into a second wash vessel, in which the pigment proper is deposited. Next, the liquid, still containing suspended particles, is run into a third vessel, where it stands till clear. At the bottom of this the finest powder is found, the so-called "*Eschel*." The pigment and the *Eschel* are washed several times, and the wash-water collected in a tank in which the so-called "tank-eschel" is deposited.

The pigment is now put into hot drying chambers, or dried in the open air in the "drying-houses."

It is only known as smalt after this drying process. During all this treatment it has lost some part of any soluble constituents, but from 0.75 to 1.25 per cent. of water-glass remains. It has a dull appearance if the percentage is too high. It forms a plastic mass when mixed with water. If left in contact with water

too long it loses its fine colour and becomes grey-blue to dirty green.

Smalt is classified by the size of the grains, as well as by its content of cobalt. Letters are used to distinguish both the qualities:—

Classification by size.

C (colour, pigment).

E (eschel).

B (Bohemian, i.e., of medium coarseness from 0·02 to 0·04 inch diam.).

H (high, i.e. largest size).

S is used to distinguish unsieved pigment.

G is used to distinguish sieved pigment.

Classification by content of Cobalt.

F (fine).

M (medium).

O (ordinary).

These letters are combined to distinguish quality; the following are examples of their use:—

FC=Fine colour. FCB=Fine Bohemian colour. ME=medium eschel. OCB=ordinary Bohemian colour. Smalts which contain more cobalt than the F quality are distinguished by doubling the letter F, and qualities poorer in cobalt than the OC qualities are distinguished by the use of indices, e.g. OC<sup>2</sup> (i.e. containing half the cobalt in the OC quality); OC<sup>4</sup> (i.e. containing a quarter of that quantity).

Ludwig has given the following analysis of smalts; (1) a coarse colour from Modum, (2) a German coarse eschel, and (3) a German coarse pale colour.

	I.	II.	III.
SiO <sub>2</sub> . . . . .	70·86	66·20	72·12
Al <sub>2</sub> O <sub>3</sub> . . . . .	0·43	0·64	1·80
FeO . . . . .	0·24	1·36	1·40
CaO . . . . .	—	—	1·92
CoO . . . . .	6·49	6·75	1·95
K <sub>2</sub> O . . . . .	21·41	16·31	20·04
Ni . . . . .	—	—	trace
As <sub>2</sub> O <sub>3</sub> . . . . .	trace	—	0·078
CO <sub>2</sub> . . . . .	—	0·25	0·46
H <sub>2</sub> O . . . . .	0·57	0·67	trace

By *Zaffre* or *Safflor* is understood a mixture of roasted cobalt ore and powdered quartz, which when melted with potash will yield blue glass. This is also an article of commerce.

### 3. THE MANUFACTURE OF OTHER COBALT COMPOUNDS

Among these may be noticed:—

Cobalt phosphate and arseniate, which are known in commerce as *red oxide of cobalt*; *cobalt bronze*, a cobalt-ammonium phosphate which produces a metallic tinsel; *cobalt-ultramarine* or *Thenard's blue*, which is a molecular mixture of alumina and an oxide of cobalt, and

*zinc green*, or *Rinmann's green*, or *green cinnabar*, a compound of zinc and cobaltous oxide.

*Cobalt-ultramarine* is made by treating a solution containing 3 parts alumina and 1 part cobalt monoxide with an alkaline carbonate; or by igniting a mixture of alum and cobalt sulphate until the whole of the sulphuric acid has been got rid of. It may also be obtained by treating solutions of cobalt nitrate with potassium phosphate, collecting the precipitate, mixing it with three times its volume of aluminium hydroxide (freshly precipitated by sodium carbonate from alum solution) and heating and drying this mixture.

*Rinmann's green* may be made by treating a solution of 1 part cobaltous chloride and 5 parts zinc chloride with potassium carbonate, washing, drying, and igniting the precipitate obtained. Another method consists in igniting a mixture of blue cobalt chloride with zinc white until no more zinc chloride volatilises. Another is to treat a solution of zinc and cobalt sulphates with sodium carbonate, wash and ignite the precipitate. It is also prepared by evaporating to dryness a solution of zinc and cobalt nitrates and igniting the residue. Or lastly, by mixing cobalt nitrate solution with zinc oxide, evaporating to dryness, and igniting the residue.

In all these cases the colour may be spoiled, and turned grey by allowing the temperature to rise too high during ignition.

# PLATINUM

## PHYSICAL PROPERTIES

PLATINUM has an almost silver-white lustre and a hackly fracture. It is ductile and malleable in a very high degree. Its hardness is equal to that of copper: its tenacity lies between those of gold and copper.

Its specific gravity is, according to Deville and Debray, from 21.48 to 21.50 at  $17.6^{\circ}\text{C}.$ ; by the addition of a certain quantity of iridium it rises to 21.8. It crystallises in the regular system. It can be welded at a white heat, and melts in the oxy-hydrogen jet at about  $1775^{\circ}$  (Violle), or according to earlier statements at about  $2000^{\circ}$ . If combined with carbon and silicon it will melt at a lower temperature.

The question of the volatility of platinum at higher temperatures has not yet been decided with certainty. It is well known that when quite pure it may be heated far above its melting point in the oxy-hydrogen blast, without any loss whatever by volatilisation. But it has been proved to be volatile when combined with silicon or carbon. Further, it is volatile in the presence of chlorine and osmium.

If quickly cooled, molten platinum is said to spit in the same way as silver. According to Heræus the spitting occurs only when oxygen is forced into the molten metal. According to Aubel the cause of the spitting is that the surface of the metal is contracted by a quick cooling, and the liquid portions underneath are forced out and burst through this cover.

At a high temperature platinum is permeable by hydrogen. Under the same conditions oxygen, chlorine, hydrochloric acid, carbon monoxide and dioxide, and steam will not pass through. It is permeable by nitrogen in small quantities, but only in the presence of hydrogen. The red-hot metal has the property of absorbing considerable quantities of hydrogen, and of retaining it on being cooled. The hydrogen is removed by heating the metal in a vacuum.

Finely divided platinum (platinum black, spongy platinum) has the property of condensing gases, especially oxygen, on its surface.

Its ductility is considerably lessened by the presence of small quantities of the other platinum metals (which are found with it in nature), such as iridium, osmium, palladium, rhodium, ruthenium. On the other hand iridium makes platinum harder, and less easily attacked by chemical agents. Silicon even in a very small quantity (one three-thousandth part) makes platinum brittle and hard.

#### CHEMICAL REACTIONS OF PLATINUM AND OF ITS COMPOUNDS THAT ARE OF IMPORTANCE IN ITS EXTRACTION.

Platinum is unalterable in air at all temperatures. In the pure state it is not attacked by sulphuric, nitric, or hydrochloric acid, cold or hot. But if it is impure or alloyed with other metals, it will be more or less acted on by acids. For instance, from its alloys containing silver, copper, lead, bismuth, and zinc it dissolves in nitric acid, forming platonic nitrate. According to Roessler<sup>1</sup> when platinum is alloyed with silver, it becomes considerably soluble in nitric acid and the residue after treatment with the acid is not metallic platinum, but rather an oxide which is soluble in hydrochloric acid. The platinum (and part of the gold) contained in the anode slimes from the Moebius parting process (see vol. i., p. 1077) are also present as compounds with oxygen (and nitrogen) soluble in hydrochloric acid. Platinum is slowly dissolved by aqua regia to form platonic chloride, and much more quickly under increased pressure.

Perfectly dry chlorine does not affect platinum at the ordinary temperature, but acts readily at a higher temperature. Platinum sponge is converted into the lower chloride at about 250° C. Solutions of chlorine, like aqua regia, act on it slowly at ordinary pressures, rapidly at higher pressures. Ferric chloride seems to dissolve platinum. There are two chlorides, platinous chloride  $\text{PtCl}_2$ , and platonic chloride,  $\text{PtCl}_4$ . Bromine does not attack it: but a mixture of bromide or hydrobromic acid with nitric acid acts readily.

It is oxidised by fused alkali, in the presence of air, and also by heating with alkali nitrates. There are two oxides,  $\text{PtO}$  and  $\text{PtO}_2$ .

When sulphur is heated with finely divided platinum in a glass tube in a vacuum, the two substances combine readily to form the monosulphide  $\text{PtS}$ . If heated to redness in the air this compound decomposes, and platinum metal remains. Another sulphide, platinum disulphide,  $\text{PtS}_2$ , is obtained by melting platinum with sulphur and

<sup>1</sup> *Chemiker Zeitung*, August 29, 1900.



an alkali, or by melting the double chloride of platinum and ammonium with sulphur. This disulphide dissolves in alkaline sulphides.

Silicon combines with platinum if the latter is heated with carbon and silica, or if heated with carbon alone in a clay crucible. By melting platinum with silicon, Winkler obtained the compounds  $\text{PtSi}_3$  and  $\text{Pt}_2\text{Si}$ . They are brittle and hard, and lose their silicon at very high temperatures.

Platinum combines with phosphorus at a red heat.

Metallic platinum is deposited from all its salts when they are heated to redness. If a solution of the chloride is treated with organic substances such as alcohol, or with magnesium, zinc, or iron, platinum separates in the form of a black powder known as platinum black.

Potassium and ammonium chlorides give with a solution of platinum chloride precipitates of the respective double chlorides. When these are heated, metallic platinum is left in a spongy form. If it is the potassium-platinum chloride that is heated, potassium chloride is left behind as well as the metal.

Platinum alloys with a large number of metals; for instance, with iridium, osmium, palladium, rhodium, ruthenium, gold, silver, copper, iron, lead.

Compact platinum does not amalgamate with mercury in the cold. When heated it forms a slight coating of mercury which is easily wiped off. However, spongy platinum takes up mercury when the two are rubbed together and gently warmed with the addition of slightly acidified water.

Since the platinum found in nature is compact, it can be separated by mercury from native gold.

If platinum is melted with lead a brittle alloy is obtained, from which lead may be driven off by cupellation. If the alloy is powdered and exposed to moist air containing carbon dioxide, the excess of lead will be oxidised away as white lead, until just enough is left for the alloy  $\text{Pt} + \text{Pb}$ , which remains. This is easily decomposed by heating with mineral acids. Thus it is possible to collect platinum by melting it in lead, and then removing the lead by cupelling.

#### ORES OF PLATINUM

Platinum is found in the native condition, and combined with arsenic, as the mineral *sperrylite*. Only native platinum is used as a source of the metal.

Native platinum is usually alloyed with the metals known as the platinum group, namely, iridium, osmium, rhodium, palladium, ruthenium, and also with iron and some copper. As much as 27·8 per cent. of iridium has been found in specimens of platinum, and 19 per cent. of iron.

Platinum is found most usually in beds of gravel and sand which have been formed by the wearing away of the original deposits containing the metal. In such secondary deposits known as "alluvials" or "placers," it is found like gold in grains and flakes, more rarely in nuggets. The chief impurities are serpentine, quartz, zircon, spinel, corundum, titanite, chrome, and magnetic iron ores, gold, and osmiridium. The largest lump of platinum found up till now in the "alluvials" of the Ural Mountains is in the Demidoff Museum at St. Petersburg, and weighs 21·64 lbs.

The most important sources of native platinum are in Russia, which country produces far more of this metal than any other. Platinum is found there in the middle Urals between 57°30' and 59°30' northern latitude, also in a tract of country 80 miles long in Perm and in the province of Ekaterinburg. The richest districts are those of Goroblagodat and Nischni-Tagilsk, where the deposits are alluvial and are found in the valleys of small streams and along the scarped hill-sides. The alluvials of Goroblagodat lie entirely on the Asiatic side of the Urals, and are found in the bed of the Iss (flowing into the Tura) and its tributary burns. They belong to Count Schuwaloff and a number of companies. The placers of the Nischni-Tagilsk district are chiefly on the European side of the Urals in the river systems of the Vissim and Martian. They belong exclusively to the Demidoff family.

The thickness of the placers proper averages 3 feet 6 inches, the cover 16 feet. Above this there is often a layer of peat. The constituents of the deposits are diorite, gabbro, diorite, olivine, diorite porphyry, pyroxene porphyry, serpentine and quartzite. The platinum comes from the basic rocks, which are rich in magnesia. It was found in serpentine rock in 1892 by Innostranzeff. It occurs without gold only in three deposits in the Tura system. All the other deposits in the Urals contain gold as well as platinum, the ratio being 1 : 6·5 on Demidoff's property, and 1 : 31 on Schuwaloff's. In recent years the platinum content of the deposits has decreased, due to the fact that the richer beds in the smaller streams were worked formerly when the price of platinum was low, but now that prices are high, the tailings from the richer deposits and the placers in the larger valleys are being treated. In the province of

Goroblagodat the richer sands still contained 31·103 grains per ton of platinum in 1870, during the decade from 1870 to 1880 15·55 grains per ton. In 1887 the platinum content of all the placers varied between 3 and 19 grains per ton; on the average 3·5. In 1894 and 1895 deposits with three grains per ton could be worked with profit, and at the high prices now ruling  $\frac{1}{2}$  grain per ton is sufficient to cover the costs of working.<sup>1</sup> Other localities for platinum are Spain, Ireland (co. Wicklow), Norway (Arendal), South America (the provinces Choco and Barbacoas in the Republic of New Granada, Minas Geraes, and Matto Grosso in Brazil), North America (British Columbia, California, especially Trinity and Shasta Co., Oregon, North Carolina, Canada, Mexico, San Domingo, Hayti), Borneo, East Indies, Lapland, Australia (Fifield, New South Wales), New Zealand. Platinum to the extent of 0·0004 per cent. has been found in the sand of the Rhine by Hopff and Döbereiner.

The alluvial soil or sand containing platinum is washed, and any gold present in the residue removed by treatment with mercury. In this condition it is sent to the platinum works for further treatment.

The composition of the platinum thus obtained, the so-called crude platinum, will be seen in the following analyses:—

	Russian platinum						Platinum from British Columbia. Analysed by Hoffman.		California. Deville.	Brazil. Svanberg.	Choco. Deville and Debray.	Borneo. Blekerode.
	From Nischni-Tagilsk in the Urala. Analysed by Kern. <sup>2</sup>			From Goroblagodat in the Urala. Analysed by Kern. <sup>3</sup>								
	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
Pt . . . .	80·87	71·20	89·05	87·50	84·50	80·05	78·48	68·19	79·85	55·44	86·20	70·21
Ir . . . .	0·08	2·43	tr.	0·05	0·90	2·50	1·04	1·21	4·20	27·79	0·85	6·13
Os . . . .	tr.	0·05	tr.	0·01	0·06	tr.	—	—	0·05	—	—	1·15
Pd . . . .	1·30	1·95	2·35	1·05	0·05	2·03	0·09	0·26	1·95	0·49	0·50	1·41
Rh . . . .	4·44	1·50	4·60	1·20	2·90	1·05	1·70	—	0·65	6·86	—	0·50
Fe . . . .	10·32	13·40	3·40	8·60	7·55	11·04	9·78	7·87	4·45	4·14	7·80	5·80
Cu . . . .	2·30	6·70	0·59	0·65	0·60	1·02	3·89	3·09	0·75	3·30	0·60	0·34
Os-Ir . . .	0·11	2·65	tr.	1·50	2·80	2·51	3·77	14·62	4·95	—	0·95	8·86
Chromite .	—	—	—	—	—	—	1·27	1·95	—	—	—	—
Ru . . . .	—	—	—	—	—	—	—	—	—	—	1·40	—
Au . . . .	—	—	—	—	—	—	—	—	0·55	—	0·95	8·97

Sperrylite,  $\text{PtAs}_2$ , is found in the copper and nickel bearing magnetic pyrites at the Vermilion Mine, Sudbury, in Canada. It has also been found recently in the copper ores at Rambler Mine, Albany Co., Wyoming,<sup>4</sup> associated with covellite, one sample

<sup>1</sup> *The Min. Ind.*, 1898, p. 541. *Min. and Sci. Press*, September 10, 1898.

<sup>2</sup> *Chem. Centralblatt*, 1877, p. 287.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *The Min. Ind.*, 1901, p. 536.

containing 12 ounces per ton. The average composition of the ores is<sup>1</sup>:—

Au . . .	0.16–0.19 ounces per ton
Ag . . .	3.8– 4.72 „
Pt . . .	0.69–0.74 „
Pd . . .	1.8– 1.9 „

The copper matte prepared from these ores contained:—

Au . . .	0.40–0.45 ounces per ton
Ag . . .	7.40–7.46 „
Pt . . .	0.99–1.05 „
Pd . . .	3.15–3.25 „

Sperrylite has also been found in the sands of Cower Creek, Macon Co., N.C.

Besides occurring native, or in alloys, platinum is found in very small quantities in fahl-ores, zinc blendes, lead, silver and uranium ores, and in various rocks. For instance, Rössler has found 0.0058 per cent. of platinum in the *Blicksilber* of Commern and Mechernich.

### THE EXTRACTION OF PLATINUM

The extraction on the large scale is preceded by a concentration of the ore by washing. If gold is present it is concentrated with the platinum by the same process. Gold is removed from the residue by mercury, which amalgamates with this metal and does not affect platinum.

In Russia the washing is done in summer, sluices being cut where water is plentiful. These are similar in construction to, though smaller than, the sluices used in California for the hydraulic mining of gold. Washing is then carried out chiefly by hand, sometimes by machines.

Washing machines with stirring arrangements are used for clayey ores. The construction of these is shown in Fig. 487. The lower part is conical in shape and made of cast iron, the upper part which fits upon it is made of wooden staves; it is cylindrical in form and 3 feet high. The bottom is perforated by holes 0.6 inch in diameter. Water is supplied in a number of streams from a circular

<sup>1</sup> *The Min. Ind.*, 1903, p. 527.

cast-iron pipe perforated with holes, which is placed at the top of the lower part of the apparatus. The stirring arrangement is in the form of an upright shaft with six arms, to which are attached vertical iron teeth reaching to the bottom of the apparatus. The shaft makes 25 revolutions in a minute. The coarser pieces of the ore

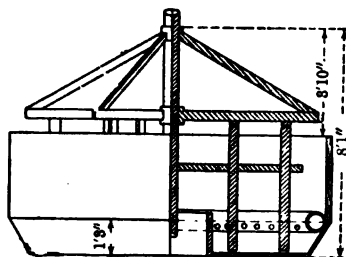


FIG. 487.

which are fed in remain in the apparatus, while the sands are washed through the perforated bottom into a trough and are there further washed as shown in Fig. 488. The larger pieces of ore which collect on the bottom of the apparatus are removed at times through a hole in the bottom and taken away in waggons. In this apparatus 200 tons of lump ore can be washed in 24 hours. The power is supplied by a steam engine of 10 to 15 H.P.

The washing machine most used in Russia is shown in Fig. 488. It consists of two cylindrical sieves and washing troughs. The former,

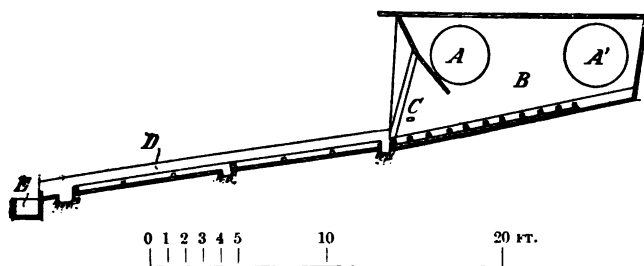


FIG. 488.

$AA'$ , are about 10 feet long and are perforated with holes about  $\frac{1}{2}$  inch in diameter. They are in a sloping position and are supplied with water at the upper ends. Sand, clay, and water pass through the perforations into the box  $B$ , while the larger pieces fall into waggons at the lower ends of the drums, and are taken away. The bottom of the box slopes at  $15^\circ$  and is divided lengthwise by a board partition.

It is closed at the front end by a wooden grid. Sides and bottom are lined with sheet iron, and the bottom is covered with straw mats held in place by wooden strips. Attached to the box outside is a gutter, *D*, 17 feet long, less inclined than the floor of the box, and with some basins and transverse slats along the bottom. At the lower end is a gutter, *E*, to carry away the barren ore. Most of the platinum, especially the larger grains, collects between the riffles on the bottom of the closed box. (The box is closed mainly to prevent theft.) Only a little platinum in a finely divided form is caught outside of the box; the quantity which escapes both box and gutter has not been determined. In 12 hours 100 tons of ore are treated, five to ten times its volume of water being requisite. The platinum sand is removed twice a day from the box after taking away the slats and opening the grid, and the mats are also washed for that purpose.

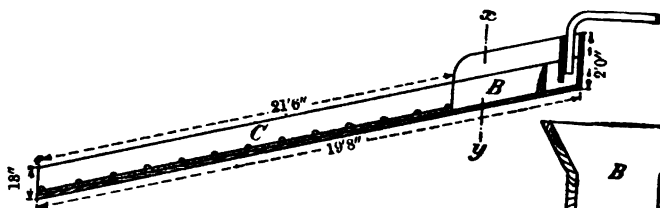


FIG. 489.

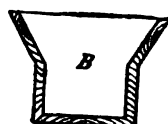


FIG. 490.

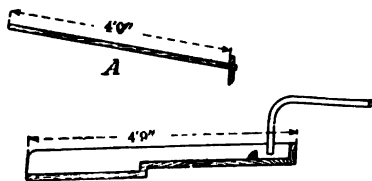
The further concentration of this sand is carried out in a trough such as is shown in Figs. 489 and 490.

The upper part of this, *B*, is lined with sheet iron. The water which enters at the head flows first downwards, then rises over a dam and escapes along the bottom of the trough. The sand is thrown in at the head of the trough and kept in agitation. The greater part of the platinum settles here; the rest, along with the barren ore, is washed away by the water and traverses the lower part of the trough *C*, which is 15 feet long. The bottom of this is lined with washed turf held in position by cross pieces. The turf between these holds back a portion of the platinum-bearing sand, which is recovered at intervals by removing the cross pieces, taking out the turf, and beating and washing it to remove the heavy particles. These are then washed again once or twice in the same apparatus.

Finally the rich sands, consisting of platinum, chromite, and other heavy minerals obtained in this way, are washed again in the small washing hearth shown in Fig. 492. This consists of two sloping

troughs 3 feet wide, one being placed below the other. The sand is charged in at the head of the trough and worked in a stream of water from the upper to the lower half by means of the agitator shown in Fig. 491. It is then taken from the trough, the gold extracted, and the residue sent to market as crude platinum.

The gold is extracted from the sand by rubbing it with quick-silver for half an hour in a dish of wood, iron or porcelain. After pouring off the amalgam the residue is treated again in the same way until all the gold has been dissolved. Russian crude platinum contains on an average 75 to 85 per cent. of platinum, along with chromite, a little iron alloyed with the platinum, up to 5 per cent. of osmium and iridium, and other metals of the platinum group like palladium and ruthenium. Most of the Russian platinum is exported, the



FIGS. 491 and 492.

greater part being taken by the firms Johnson, Matthey and Co., London, Demontis, Lemaire and Co., Paris, and Heraeus and Co., Hanau. What is not exported is refined at the works of Kolbe and Lindfors, and of Teuteleff, both in St. Petersburg.

The metallurgical treatment of platinum may be conducted either in the dry or the wet way. The dry way does not produce pure platinum, but its alloys with iridium and rhodium. The production of pure platinum requires the use of a wet method. Electrolysis is used to separate metallic platinum from its alloys with gold.

The wet method is principally used.

#### EXTRACTION OF PLATINUM IN THE DRY WAY

Two methods have been elaborated by Deville and Debray.<sup>1</sup> One consists in melting the ore in a vessel made of lime, and repeatedly remelting the button thus obtained: the second method is to melt the ore with galena and litharge in a reverberatory furnace, and scorify the lead-platinum alloy obtained in order to remove the lead. Lastly the platinum is fused into an ingot in the lime furnace.

<sup>1</sup> Dingler, vol. 153, p. 38; vol. 154, pp. 130, 199, 287, 383; vol. 165, pp. 198, 205.

The melting of the ore in this lime vessel, known as the Deville furnace, is achieved with the help of an oxy-coal-gas flame.

The arrangement of this method of melting is shown in Fig. 493.

The vessel consists of two halves formed out of a hollow cylindrical block of calcined lime. In the hollow *b* the ore is placed, through an opening in the upper half, not visible in the figure. This opening is closed by a lime stopper during the melting. A second conical opening *q* serves to admit the current of gas. This latter is led to the opening through a platinum tube which has a perforated tip at its lower end. This tube is attached at its upper end to a copper one, *e*. Through the tube *h*, the coal gas, and through the tube *o*, the oxygen are introduced. The products of combustion escape through the opening *d*; the same opening serves for pouring the molten mass. There is a proper arrangement of taps to both gas pipes, so as to make the flame oxidising or reducing.

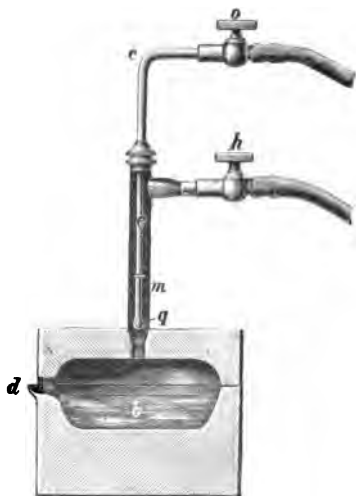


FIG. 493.

After a small portion of the ore, previously warmed and mixed with some lime, has been put in through the opening mentioned, it is melted in an oxidising flame. Metals other than the noble ores are thus oxidised and form, with the lime and any gangue present, a slag, which is absorbed by the lining of the vessel.

Any volatile compounds or powdery substances escape with the products of combustion.

To this molten mass ore is now added in small portions until the lower part of the cavity is filled with molten metal. It is then poured out and remelted in another Deville furnace with an oxidising flame, so that again part of the commoner metals are oxidised and absorbed by the lime. The continual use of a fresh furnace is rendered necessary by the decreasing power of absorption of the lime for the slag. Finally, there is obtained, not pure platinum, but an alloy with iridium and rhodium, from which pure metal can be obtained by a wet method.

The second method by Deville and Debray separates platinum from the ore by the help of lead, which alloys with platinum but not with osmiridium.



## PLATINUM

For this purpose about 1 cwt. of the crude platinum is in a reducing flame, with the same quantity of galena, in a smelting furnace, on a hearth composed of marl or calcium plaster, about 3 feet 3 inches long, 6 inches medium depth, and 2 feet broad. The galena is decomposed by the iron present in the lead, a lead matte is formed and metallic lead set free, which is alloyed with platinum. To decompose the matte about 2 cwt. of litharge are added, the heat increased and the whole covered with a layer of glass. The lead matte is reduced to lead by the litharge, which again forms the platinum alloy, while sulphur dioxide

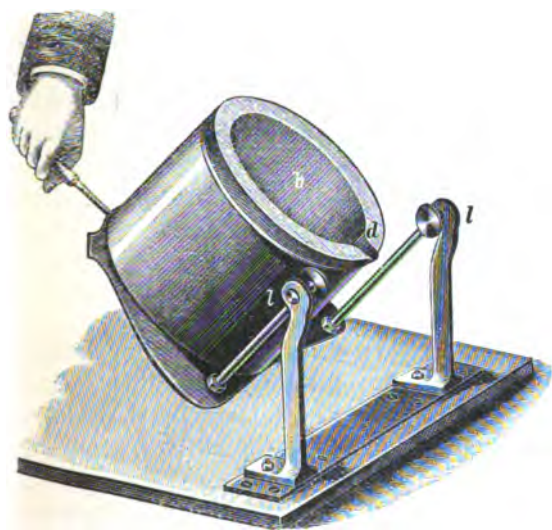


FIG. 494.

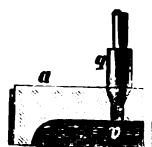


FIG. 495.

off. Osmiridium, which does not alloy with lead, remains at the bottom of the furnace. After the slag containing lead has been skimmed off, the alloy is removed by a cast-iron ladle. The residue of the bath containing the osmiridium is added in the next step of another portion of ore, so as to enrich it. Finally, this portion is poured out on to a gently sloping surface, on which the osmiridium remains, while the platinum-lead alloy runs away.

The former is removed to a refining furnace provided with a blast. In proportion as the lead is removed the temperature must be further raised. It is not, however, possible to remove the whole of the lead while the material remains liquid, as it solidifies before the lead is still present.

The residue is melted in the Deville furnace already described.

in this the lead and any other volatile elements are volatilised away, and the commoner metals are oxidised, and passed into slag. Rhodium and iridium remain with platinum. The platinum is poured into moulds lined with sheets of the metal.

To melt larger quantities of platinum (more than 9 lbs.), the vessel shown in Figs. 494 and 495 is used. It consists of a cylinder of sheet-iron lined with lime, and with the cover shown in Fig. 495. A stream of oxy-coal-gas is led through the hole in this cover. The vessel can be tipped to pour out platinum. In this Deville and Debray melted about 25 lbs. of Russian coins with the use of 4.2 cubic feet of oxygen.

The Siemens electric furnace, which was expected to be of great service in fusing platinum, has not fulfilled expectation, because platinum always absorbs carbon from the carbon electrodes of the furnace, and thus loses most of the properties that are of value in the arts.

Up to the present time the dry method of obtaining platinum has only been used exceptionally.

#### EXTRACTION OF PLATINUM BY WET METHODS

This method of extraction consists essentially in bringing platinum into solution with aqua regia, precipitating from this solution platinum-ammonium chloride by means of ammonium chloride and ammonia, and then decomposing this compound and separating platinum at a red heat.

This process, invented by Wollaston, was formerly carried out with slight variations at the laboratory of the Department of Mines at St. Petersburg. There the ore was treated for 8 or 10 hours in open vessels, on a hot sand-bath, with 10 or 15 times its weight of aqua regia (composed of 3 parts hydrochloric acid at 25° B. and 1 part nitric acid 40° B.). By this means platinum, a portion of its kindred metals, and baser metals were brought into solution, while osmiridium chiefly, with rhodium and ruthenium, and small quantities of iridium and palladium, remained behind with the sandy residue.

The solution which contained besides platinum, iridium, rhodium, palladium, copper, iron, and small quantities of osmium and ruthenium, was treated with solution of sal-ammoniac in glass vessels to precipitate the platinum as double chloride. In this process it was necessary for the solution to contain excess of acid to prevent a precipitate of iridium from coming down.

The precipitate of double chloride was washed and dried and

strongly heated in platinum vessels, whereby it is converted into platinum sponge. This sponge is triturated, sieved, pressed together in a screw press with steel dies, and then strongly heated for  $1\frac{1}{2}$  days in a porcelain furnace. This red-hot platinum was hammered into bars or rolled into sheets.

The first part of the wash-water obtained in washing the platinum-ammonium chloride precipitate was evaporated down to one-twelfth its original volume, when a similar iridium salt containing platinum crystallised out, and, on heating, yielded a platinum-iridium alloy. The second part of the wash-water was evaporated completely to dryness, heated to redness, and added to a fresh portion of ore when the latter was treated with aqua regia.

Since the platinum obtained in this process was not free from iridium, Döbereiner's<sup>1</sup> method to obtain platinum without iridium was used. The platinoid metals, but not platinum itself, are precipitated by treating the aqua regia solution diluted to 35° B., with lime water until the reaction is only feebly acid, light being excluded during the process. But this process gave neither a precipitate of the platinoid metals free from platinum, nor platinum free from them.

Schneider,<sup>2</sup> in order to avoid the precipitation of iridium with platinum, treats the ore with aqua regia and excess of hydrochloric acid, and evaporates the solution obtained nearly to dryness. The liquid is then diluted with water, treated with soda until it is fairly alkaline, and boiled with alcohol. The precipitate obtained is dissolved in hydrochloric acid. From this solution platinum can be precipitated by ammonium chloride as the pure double chloride. By this method iridium and rhodium are converted into sesquichlorides, which are not precipitated by sal-ammoniac. According to Louis,<sup>3</sup> the method at present used in Russia is to dissolve the crude platinum in aqua regia, a porcelain basin heated on a sand-bath being used for that purpose. The solution is taken down to dryness, the residue dissolved in hydrochloric acid and evaporated to dryness, and this process is repeated until the solution is free from nitric acid. It is now filtered from the insoluble sand, chromite, platinum metals, &c., and sold to German works, where it is treated for the platinum metals. The platinum is precipitated in glass vessels with ammonium chloride and the crystals, decanted from the mother liquor, washed in a bowl-shaped filter, a pump being used to quicken the process. In this way ammonium platini-chloride is obtained in cakes about 1 foot in diameter and 3 inches thick. These are

<sup>1</sup> Liebig's *Annalen*, vol. xiv., pp. 10, 251.

<sup>2</sup> Dingl. vol. exc., p. 118.

<sup>3</sup> *The Min. Ind.*, 1898, p. 551.



slowly dried and then heated in a muffle on a sheet of platinum up to redness, ammonium chloride and chlorine being driven off, and a residue of spongy platinum being left as a grey cake. This is then powdered, compressed in a mortar with a steel pestle, and melted down with the oxy-hydrogen blow-pipe flame in a Deville furnace (Fig. 493). The furnace is made of sawed-out blocks of calcareous tuff held together by iron bands. A small furnace holding 7 to 10 lbs. of platinum and heated with one blow-pipe is made from a single block 8 by 8 inches in horizontal section and 10 inches high. The larger furnaces hold 33 to 40 lbs. of platinum and are heated by two or three burners. They rest upon iron plates and can be tipped to pour the metal. The moulds are of the same material as the furnaces, and the ingots produced are about 2 inches thick. Each furnace can only be used for one melting.

The filtrate from the ammonium platinichloride still contains platinum, and this is precipitated by means of iron. The metal thus obtained is impure and is treated in the same way as the crude platinum. The ingots are heated to redness and then rolled into plates half an inch thick.

Heraeus in Hanau,<sup>1</sup> in order to make the ore dissolve more quickly, places it in glass retorts with a mixture of 1 part aqua regia with 2 parts water, under a pressure of 12 inches of water, evaporates the solution, and heats the residue obtained to 125°, so that the sesquichlorides of iridium and palladium are formed. Then this residue is dissolved in hydrochloric acid. Next the pure double chloride is precipitated from the solution. This is converted into platinum sponge by ignition, and the sponge melted in a lime crucible. The liquid filtered from the platinum double chloride precipitate is evaporated to a certain density, when the iridium salt comes down. The remaining metals are precipitated from this solution by iron turnings. The excess of iron is removed from the precipitate by hydrochloric acid, and the latter is then treated with aqua regia in order to obtain more of the platinum and iridium precipitates.

Palladium, rhodium, ruthenium, osmium, and iridium may be obtained from the residues after the ore is dissolved, and from the mother liquors after precipitation.

G. Matthey<sup>2</sup> produces pure platinum from the commercial crude metal by melting it with six times its amount of lead, granulating

<sup>1</sup> *Amtl. Bericht über die Wiener Weltausst. i. J.*, 1873, vol. iii. 999. *Dingl.* vol. ccxx., p. 95.

<sup>2</sup> *Chem. News*, 1879, xxxix. No. 1,013, p. 175. *Berg- und Hüttenm. Ztg.*, 1880, p. 28.

this alloy, and treating it with dilute hydrochloric acid, which dissolves iron, lead, palladium, and rhodium, while platinum remains behind with iridium, and small quantities of lead, rhodium, and other platinoid metals. This residue is boiled with aqua regia, when platinum and lead dissolve and iridium remains behind. The lead is precipitated by sulphuric acid. The liquid is filtered from lead sulphate and treated with excess of ammonium chloride and common salt to precipitate platinum in the usual way. If rhodium is present in the solution, the precipitate is rose-colour instead of pure yellow. It is ignited with bisulphate of potash, which forms rhodium-potassium sulphate, while the platinum separates as metal. The double salt is dissolved by boiling the whole with water.

To hasten the separation of platinum and minimise the quantity of aqua regia, it has been proposed by Hess,<sup>1</sup> and by Dullo,<sup>2</sup> to melt crude platinum with four or five times its weight of zinc, and treat the alloy with sulphuric acid first.

Wyott<sup>3</sup> has brought forward a process for extracting the platinoid metals from residues and mother liquors. Platinum, palladium, and rhodium are dissolved out of the ores by aqua regia. The first is precipitated by ammonium chloride. The liquid is filtered off, neutralised by soda, and palladious cyanide ( $\text{PdCy}_2$ ) precipitated from it by mercuric cyanide. Rhodium remains in the solution. The residue after treatment with aqua regia is to be heated in a stream of air, whereby osmium is converted into tetroxide, which volatilises, and rhodium oxide is deposited in the hotter parts of the outlet tube. The residue, after this heating, is mixed with salt, and heated in a stream of chlorine. Sodium-iridium chloride is formed, which is dissolved by boiling water.

When gold is precipitated from an aqua regia solution by ferrous chloride (described under Gold<sup>4</sup>), the solution which remains consists of iron chloride, which, together with finely divided gold, in many cases contains also platinum, palladium, and chloride of silver finely divided, while iridium, ruthenium, rhodium, selenium, and various base metals are in the solution. From these materials platinum and the platinoid metals are extracted at the gold and silver works at Frankfort-on-Main by the following process.<sup>5</sup>

Sheet iron cuttings are first placed in the solution in order to reduce ferric to ferrous chloride, which can be used again to precipitate gold. The iron throws down selenium and the metals mentioned, in the form of a black mud, which is removed from time

<sup>1</sup> *Erdm. Journ.*, vol. xl., p. 498.

<sup>2</sup> *Ibid.*, vol. lxxviii., p. 369.

<sup>3</sup> *Eng. and Min. Journ.*, 44, p. 273.

<sup>4</sup> See vol. i., pp. 994 *et seq.*

<sup>5</sup> *Ding. Polyt. Journ.*, 224, p. 414.

to time from the vessels (large stoneware pots). After the larger pieces of iron have been sieved out of the mud, it is digested with ferric chloride to remove iron and copper, and then repeatedly washed with dilute hydrochloric acid. It is next dried and smelted with soda and coal. A button of metal is obtained, and a slag containing selenium, which is collected and worked up for that element. The metallic button is re-melted and granulated, then digested in glass retorts with aqua regia containing excess of hydrochloric acid, by which means the greater part of any copper present is removed. It is necessary for this purpose to use a limited quantity of the acid mixture, as otherwise copper and all the noble metals will be dissolved, and the presence of copper will make the precipitation of platinum and palladium difficult. The noble metals that pass into solution are separated again by the metallic copper still remaining in the granules or by copper wire put in for the purpose. Finally, the solution contains principally cuprous chloride, kept dissolved by the excess of hydrochloric acid, and also some cupric chloride. After the metallic mud has been nearly freed from copper by this operation, repeated if necessary, it is boiled with aqua regia, and all the metals brought into solution. When this is diluted with water, antimony is thrown down as oxychloride. The diluted solution is afterwards brought back to its former concentration by evaporation, and the gold is thrown down electrolytically. (Gold must not be thrown down by ferrous chloride, which would bring back iron into the solution.) Next, platinum is precipitated by sal-ammoniac, and the precipitate, after ignition, gives the metal with only 0.005 per cent. impurity. The filtrate from this last precipitate still contains sal-ammoniac, and is used to precipitate platinum from another solution, whereby the quantity of iridium and palladium dissolved in it is increased. Afterwards, this enriched solution is evaporated until the iridium-ammonium chloride separates out, and lastly, from this mother liquor the similar palladium double salt is crystallised out by adding ammonia and hydrochloric acid.

The usual composition of platinum metal is given by the following analyses<sup>1</sup> :—

	I.	II.	III.
Pt . . . . .	99.29	99.9	99.9
Ir . . . . .	0.32	—	—
Rd . . . . .	0.13	0.01	—
Pd . . . . .	—	—	—
Ru . . . . .	0.04	—	—
Fe . . . . .	0.06	—	0.0001
Cu . . . . .	0.07	—	—
As . . . . .	—	0.01	—

<sup>1</sup> *Mineral Industry*, 1892, p. 384.

The origin of the first sample is unknown; the second is from Johnson, Matthey and Co.'s works in London, and the third from the works of Heræus in Hanau.

#### EXTRACTION OF PLATINUM BY AN ELECTRO-METALLURGICAL METHOD

Electro-metallurgical methods have been proposed for the extraction of platinum from its ores, but never put into practice, although by these means platinum and its allied metals are separated from their alloys with gold. Further, platinum can be separated from iridium and rhodium by a weak current acting on an acid solution of platinum chloride as the electrolyte. As, however, platinum separates easily from most of its compounds by simple heating, the electrolytic method seems unnecessary in this case. The separation of gold and the platinum metals is carried out on a large scale at the North German Refinery at Hamburg.

The anodes are sheets of the impure gold, containing platinum and the metals of that group along with silver, copper and other metals; the cathodes are of gold foil, and the electrolyte is a solution of gold chloride containing excess of hydrochloric acid, or of metallic chlorides which form double salts with gold chloride, the excess of these materials and the right concentration of the gold being kept up by addition of the necessary reagents.<sup>1</sup>

Most of the constituents of the anodes pass into solution with the gold during electrolysis, but only the gold is deposited at the low tensions adopted. Platinum, though not soluble of itself, becomes so when alloyed with gold, but it is not electrolytically deposited from solution along with the gold. It is thus possible to enrich the electrolyte in platinum; and the same may be said with regard to palladium. The remaining metals of the platinum group are not dissolved, but they collect in the anode slimes together with a portion of the gold itself. Silver is separated as chloride at the surface of the anode, and falls likewise to the bottom of the bath. Although silver chloride is somewhat soluble in hydrochloric acid, yet none of the silver is deposited at the cathode, where the gold deposit seldom contains less than 99.98 per cent. of gold.

If a solution of gold chloride ( $\text{AuCl}_3$ ) free from acid be employed as electrolyte, then the chlorine liberated at the anode does not attack the gold, but is evolved in the gaseous condition. If, on the

<sup>1</sup> Ger. Pat., April 16, 1896, No. 90276. Additional Patent, June 9, 1896, No. 90511.

other hand, acid solutions of gold chloride are used, and the quantity of hydrochloric acid is kept constant, then both anode gold and platinum are brought into solution.<sup>1</sup> Wohlwill explains this phenomenon by assuming that the gold of the anodes only dissolves when the surrounding electrolyte contains chlorides suitable in kind and concentration for the formation of the ions  $\text{AuCl}_4$ . The current density is 830 ampères per square yard and the tension of the bath 1 volt. Platinum is extracted from the electrolyte by the wet methods described above.

<sup>1</sup> *Zeit. für Elektrochemie*, vol. xvi. p. 379 ; vol. xvii. p. 402 ; vol. xviii. p. 421.



# ALUMINIUM

## PHYSICAL PROPERTIES

ALUMINIUM has a tin-white colour and high lustre. If a minute quantity of silicon has been allowed to remain in it, the colour has a bluish tinge; a larger quantity makes it grey. Mechanical treatment also produces a bluish tinge.

The fracture of cast aluminium shows a coarse fibre and irregular grain, while it is fibrous or fine-grained, and shows a high silky lustre after being hammered and rolled.

According to Deville, aluminium crystallises in regular octahedra if slowly cooled. According to Rose the crystals do not belong to the regular system.

The specific gravity of aluminium is considerably less than that of all other metals used generally in commerce. It is 2.58 for the pure metal, and from 2.60 to 2.74 for the commercial metal, according to the treatment it has undergone.

Both pure aluminium and the commercial metal (98.5 per cent.) can be wrought, drawn, and rolled in the cold. The greatest ductility is at 200° C. When worked in the cold it loses ductility, but this is restored by annealing. If the metal contains 97 per cent. of aluminium and 3 per cent. of heavy metals and silicon, it can only be rolled in the cold by repeatedly annealing it. If it contains 5 per cent. of impurities, including silicon, it can only be worked when hot, and the temperature then should not exceed 350° to 400° C. Forging and rolling are best done at 200° C. It is best worked in the press at 500° C. At 550° C. it becomes pasty and breaks into pieces under the hammer.

By working aluminium in the cold its hardness and tenacity are increased, its ductility diminished. As the temperature rises the tenacity diminishes. The tensile strength of cast aluminium is 17,042 lbs. per square inch with 3 per cent. extension. This is

increased by cold rolling and hammering. By slight reduction of its cross section the tensile strength is brought to one and a half times the above amount. Reduction in the ratio of 20:1 brings up the tensile strength to about twice the first value with an extension of 4.3 per cent.; and reduction in the ratio of 80:1 to 39,200 lbs. per square inch with an extension of 4.2 per cent.

Aluminium wire  $\frac{1}{16}$  inch in diameter had, when warmed, a tensile strength of 35,500 lbs. per square inch.

The electrical conductivity of aluminium (that of copper being taken as 100) is as follows:—<sup>1</sup>

Aluminium Content of Metal.	Conductivity.
98.5 per cent.	55
99       "       "	59
99.5       "       "	61
99.75       "       "	63 to 64
100       "       "	probably 66 to 67.

The thermal conductivity is 31.33, that of silver being taken as 100. The coefficient of linear expansion is 0.0023 or  $\frac{1}{433}$  at 100° C. The specific heat is 0.2220 at 0° C., and 0.2270 (average) between 0° and 100° C., and 0.275 at the melting point.

Aluminium melts at a red heat between 600° and 700° C. (625° according to Le Chatelier). Its latent heat of liquefaction is 100 Cal. It volatilises at a high temperature, though at what point has not been determined. It has a high specific heat, so that much heat and time are needed to liquefy a large quantity of the metal; in like manner as the latent heat of liquefaction is great, the molten metal takes a long time to cool down and solidify. According to Deville many hours elapse before a small ingot freshly poured becomes cool enough to take into the hand. There is a contraction in volume of the metal as it passes from the liquid to the solid state, the amount being 1.7 per cent. of the original volume.

Aluminium is distinguished by a clear ringing sound when struck.

#### CHEMICAL PROPERTIES OF ALUMINIUM AND OF ITS COMPOUNDS WHICH ARE IMPORTANT IN ITS EXTRACTION

Compact aluminium does not oxidise in either wet or dry air at the ordinary temperature. When melted it oxidises very slightly and becomes covered with a thin deposit of alumina, which prevents further action. It is, however, easily oxidisable when in

<sup>1</sup> Richards, *Franklin Journ.*, 1897, p. 143.

fine division or in thin leaves; it then burns, if heated in a gas-flame, with a dazzling light, and forms the sesquioxide. If it is fused with saltpetre, it is not oxidised at a dull red heat, but forms potassium aluminate when further heated. At a strong white heat it burns superficially to form the sesquioxide, but here again a thick layer of this oxide stops further action.

When melted it reduces many oxides, for example, those of iron, lead, copper, carbon, silicon, and boron, forming alumina. Any aluminium remaining combines with the element thus separated. Alumina, the sesquioxide, is not soluble in metals, and does not deteriorate them when present; therefore aluminium forms a good agent for purifying metals containing their oxides, and superior to other elements similarly used for refining (such as silicon, phosphorus, manganese, magnesium, and sodium).

Aluminium is not attacked by water, either when boiling or at the ordinary temperature. At a red heat steam hardly attacks it; at a white heat it is only superficially and slightly oxidised.

Mylius and Rose<sup>1</sup> find that water containing air acts upon aluminium so that small quantities of hydrogen peroxide are formed which disappear during the oxidation of the metal.

At a high temperature sulphur combines directly with the metal to form the sulphide ( $\text{Al}_2\text{S}_3$ ), but sulphuretted hydrogen has no action on it. In this respect aluminium has an advantage over silver, which is blackened by sulphuretted hydrogen, the sulphide being formed.

Chlorine, bromine, iodine, boron, and silicon combine easily with aluminium.

It is hardly attacked by dilute sulphuric acid, but dissolves slowly in the hot concentrated acid.

Nitric acid has little action on it. Hydrochloric acid dissolves the metal more easily in proportion as it is more concentrated; it therefore forms the best solvent. Potash and soda lye dissolve the metal energetically; hydrogen is given off and potassium or sodium aluminate formed. Fused alkalis, with not more than one equivalent of water, do not attack aluminium.

Aqueous ammonia attacks it only slightly, gaseous ammonia not at all. Organic acids have no action in the cold, and only a very feeble one when warmed.

Finely divided aluminium will burn with flame in a stream of chlorine, forming the chloride. Carbon monoxide attacks aluminium at a high temperature, according to Guntz and Masson,<sup>2</sup> and in the

<sup>1</sup> *Zeitschr. f. Instrum.*, 1893, p. 77.

<sup>2</sup> *Pariser Akademie der Wissenschaften.*

presence of a little iodide or chloride of the metal, alumina and aluminium carbide being formed.

A solution of aluminium chloride acts energetically on the metal, forming a basic chloride. A solution of alum mixed with common salt dissolves aluminium, giving off hydrogen, and forming a basic chloride.

Aluminium precipitates most metals from the solutions of their salts, and it separates silver, lead and zinc from alkaline solution of these metals.

Amongst the materials used as fluxes, carbonates and sulphates of alkalies, also silicates and borates, are found to have a specially injurious effect on aluminium. Silicon and boron will be set free from the two last; and silicon combines in all proportions with aluminium, and is always taken up, if excess be present. Silicates and borates should, therefore, not be present during the production of the metal. Haloid compounds of aluminium attack the metal. The least injurious fluxes are common salt and calcium fluoride.

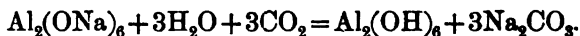
It is therefore best to fuse aluminium without any flux.

#### ALUMINIUM OXIDE: ALUMINA ( $\text{Al}_2\text{O}_3$ )

is found naturally as corundum, sapphire and emery. It is obtained artificially, by igniting the hydrate, in the form of an amorphous white powder, which is insoluble in water, and difficultly soluble in acids. It may also be obtained in the same form by igniting aluminium sulphate, and ammonia-alum. It melts at a very high temperature to a clear, colourless liquid, which is split up by an electric current into aluminium and oxygen. It is reduced to metal by carbon at the high temperature of the electric current. It acts as acid radicle to many bases (alkalies and alkali earths), and forms aluminates. The best known is sodium aluminate,  $\text{Al}_2(\text{NaO})_6$ .

Alumina forms several hydrates with water, from  $\text{Al}_2\text{O}_3(\text{OH})_2$  to  $\text{Al}_2(\text{OH})_6$ .

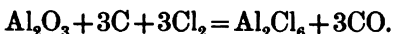
These hydrates occur naturally as diaspore, bauxite and hydrargillite. Artificially, a hydrate is obtained by precipitation from an alkali aluminate with carbon dioxide. Thus with sodium aluminate:



This gives a loose white powder soluble in acids. It acts as an acid with oxides of the alkalies and alkali earths.

ALUMINIUM CHLORIDE( $\text{Al}_2\text{Cl}_6$ )

is obtained by burning the metal in chlorine. In Oerstedt's method it is obtained by igniting an intimate mixture of alumina and charcoal in a stream of chlorine :



If the hydrate is dissolved in hydrochloric acid and the solution evaporated, the anhydrous chloride cannot be obtained, as the solution splits up into alumina and hydrochloric acid. Aluminium chloride is colourless, gives off vapours in the air, and absorbs moisture from it. At high temperatures (below its melting point), it volatilises easily. If these vapours act upon aluminium at a red heat in an atmosphere of oxygen the oxychloride is formed. If aluminium is heated to  $1300^\circ \text{C}.$ , in a tube containing vapours of the chloride in the absence of air, small drops of the fused metal are deposited in the cool parts of the tube (Troost and Hautefeuille). The explanation seems to be that a gaseous lower chloride is formed, and then decomposed.

Aluminium cannot be successfully separated from the chloride by an electric current, because this compound volatilises before it fuses. The decomposition goes on properly, however, if the easily fusible double chloride with sodium is used. This double salt was formerly used to obtain the metal. Aluminium fluoride can be obtained according to Grabau, by decomposing cryolite ( $\text{Al}_2\text{F}_6 \cdot 6\text{NaF}$ ) with aluminium sulphate, sodium sulphate being formed at the same time. The substance obtained is a white powder, insoluble in water. It is decomposed by sodium at a red heat, aluminium in the metallic form being deposited while an artificial cryolite (aluminium and sodium fluoride) is formed. Grabau bases his method for extracting aluminium upon this reaction.

## ALUMINIUM SULPHIDE.

This is obtained by the action of sulphur vapour upon a mixture of alumina and carbon heated to whiteness, or by the direct union of sulphur and aluminium at a high temperature. The molten compound ( $\text{Al}_2\text{S}_3$ ) is decomposed into its constituents under the action of an electric current, though heat alone, even from electric sources, has no decomposing action upon it (Mourlot).<sup>1</sup>

<sup>1</sup> *Compt. rendus*, 1897, 124. I. 768.

## ALUMINIUM CARBIDE.

Moissan<sup>1</sup> has recently succeeded in making a compound of the formula  $C_3Al_4$ , by heating the elements in an electric furnace in an atmosphere of hydrogen. The substance forms yellow transparent crystals.

According to Borchers,<sup>2</sup> when alumina and carbon are heated in an electric furnace, a grey sintered mass is obtained, which, when cold, is brittle and crumbling, and consists of aluminium, aluminium carbide, carbon, and various impurities derived from the source of carbon.

Salts in which aluminium acts as a base are derived from the oxide  $Al_2O_3$ . The metal is not precipitated by other metals from the aqueous solutions of these salts. It has not so far been separated by an electric current.

## ALUMINIUM SILICIDE

is obtained when aluminium is melted with silicates. In this way a compound containing 70 per cent. silicon can be obtained. A portion is dissolved in the aluminium, and another part seems to be mechanically mixed like graphite in pig-iron. When aluminium silicide is treated with hydrochloric acid, part of the silicon escapes as siliciuretted hydrogen, another passes into solution as silica, and a third part remains behind as a black powder.

## ALLOYS OF ALUMINIUM.

Aluminium alloys with most metals. It combines easily with potassium and sodium. An alloy containing only two per cent. sodium decomposes water.

It also alloys readily with magnesium.

Alloys containing 10 to 12 per cent. of magnesium can be worked in every way. Mach's magnalium<sup>3</sup> belongs to this class. More than 15 per cent. of magnesium makes the alloys brittle. With 50 per cent. of magnesium the alloy breaks between the fingers, and can be powdered.<sup>4</sup>

Antimony alloys easily with aluminium in all proportions (Roche).<sup>5</sup> Alloys with less than 5 per cent. of antimony are harder, tougher, and more readily forged than pure aluminium itself. The greater the quantity of antimony, the harder and more brittle become

<sup>1</sup> *Zeitschr. für Elektrotechnik und Elektrochemie*, 1894, vol. vi.; *Compt. rendus*, vol. cxix., 1894, part i., p. 16.

<sup>2</sup> *Elektrometallurgie*, p. 98.

<sup>3</sup> Ger. Pat. 105502 and 113935.

<sup>4</sup> Minet, *Die Gewinnung des Aluminiums*. Halle a. S., 1902, p. 94.

<sup>5</sup> Minet, *op. cit.*

the alloys and the melting point rises in proportion. According to van Aubels the alloy Al Sb melts at 1078–1080° C.<sup>1</sup> The melting point of magnalium is raised by addition of up to 30 per cent. of antimony (Mach).<sup>2</sup>

Nickel readily forms alloys with aluminium which are harder and more easily worked than aluminium itself. Those with 3 per cent. of nickel can be readily moulded into plates. According to Margot,<sup>3</sup> alloys with 18 per cent. of aluminium and 82 per cent. of nickel are as hard as steel, readily polished and easily worked with the hammer.

Cobalt-aluminium alloys with 6 per cent. of cobalt can be easily rolled. An alloy prepared by Margot with 20 to 25 per cent. of aluminium and 75 to 80 per cent. of cobalt had the hardness of hardened steel, broke under the hammer, and fell to dust a few days after its preparation.

Zinc is readily alloyed with aluminium and makes the latter hard. More than 3 per cent. of zinc gives a brittle alloy.

Cadmium-aluminium alloy is fairly extensible and is used as a solder. Bismuth-aluminium alloy is brittle even with 1 per cent. of bismuth. Lead can be only imperfectly alloyed with aluminium.

Silver-aluminium alloy with 5 per cent. of silver is as easily forged as pure aluminium. Alloys of 2 parts of aluminium and 1 part of silver are easier to coin than copper silver alloys.

Gold can be alloyed with aluminium to the extent of 10 per cent. without the alloy becoming brittle (Tissier). An alloy with 22 per cent. of aluminium and 78 per cent. of gold prepared by Roberts-Austen was purple in colour and had a ruby-like lustre.

Mercury unites slowly at 100° C. with aluminium, but very rapidly at the boiling point of mercury. According to Baille and Ferny<sup>4</sup> the amalgam Al<sub>2</sub>Hg<sub>3</sub> is formed on bringing the two metals together.

Zinc-aluminium alloys are less extensible and are weaker than pure aluminium. Alloys with 10 per cent. of zinc are said to be soldered as easily as brass.

Alloys of iron, silicon and aluminium are obtained according to Minet (*op. cit.*), by the reduction of white or crude bauxite, or a mixture of these in the electric furnace. Alloys of the following compositions are known:—

	I.	II.	III.
Al . . . . .	90	85	80 per cent.
Fe . . . . .	7	10	14 „
Si . . . . .	3	5	6 „

<sup>1</sup> *L'Electrochimie*, 1901, p. 136.

<sup>2</sup> Minet, *op. cit.*, pp. 92, 97.

<sup>3</sup> Minet, *op. cit.*, p. 97.

<sup>4</sup> Minet, *op. cit.*, p. 101.

Copper and aluminium form alloys in all proportions. Copper containing up to 10 per cent. aluminium is distinguished by great hardness, strength, and tenacity, and, under the name of aluminium bronze, has found manifold technical uses, as in the preparation of optical instruments, ornaments, armour plates and propellers.

If the copper contains more than 10 per cent. of aluminium, the alloy will be brittle. Below 10 per cent. the tenacity increases rapidly. Bronzes containing more than 10 per cent. of aluminium are not made for practical purposes. The commonest bronzes contain 2.5, 5, 7.5, 9 and 10 per cent. of aluminium. Those with 9.62 per cent. correspond to the formula  $\text{Cu}_2\text{Al}$ ; those with 5.05 per cent. to  $\text{Cu}_3\text{Al}$  and those with 2.59 per cent. to  $\text{Cu}_{16}\text{Al}$ .

The colour of the bronze is bluish-white if there is more than 20 per cent. of aluminium; with between 20 and 15 per cent. of this metal it is pure white; with less proportion of aluminium it gradually becomes yellow; 5 per cent. gives a gold yellow; 3 per cent., a red gold colour.

The melting point of bronze with 10 per cent. of aluminium is about  $950^\circ$ ; it makes good castings. The toughness of aluminium is increased by an amount of copper not exceeding 6 per cent. The experiments of Charpentier Page<sup>1</sup> showed the following breaking-strains for wires 0.08 inch in diameter:—

No.	Percentage of copper.	Extension (per cent.).	Breaking strain (lbs. per sq. inch).
1 . . .	3 . . .	21.3 to 21.7 . . .	28,960 to 29,500
2 . . .	3 . . .	3.6 „ 4.5 . . .	49,260 „ 50,100
3 . . .	6 . . .	16.2 „ 20.0 . . .	31,800 „ 35,200
4 . . .	6 . . .	2.3 „ 2.8 . . .	60,900 „ 64,200

Nos. 1 and 3 were specimens of heated wire, 2 and 4 of hard wire. Thus, aluminium-copper alloys often surpass pure aluminium in respect of tenacity.

Aluminum alloys also with platinum, palladium, manganese, chromium, tungsten and titanium: further information on the alloys of aluminium is given in Joseph W. Richards' *Aluminium*, London, 1896, and in Adolph Minet's *The Extraction of Aluminium*.

#### MATERIAL FOR THE EXTRACTION OF ALUMINIUM

Aluminium, after oxygen and silicon, is the most abundant element on the globe; yet there are very few minerals which lend themselves to its extraction.

<sup>1</sup> Minet, *op. cit.*, p. 97.



The most important are bauxite and cryolite; those of secondary importance are rocks containing aluminium sulphate, kaolin and clay. Hydrargillite and diasporé,  $\text{Al}_2(\text{OH})_6$ , are not used in the preparation of the metal owing to their scarcity.

*Bauxite* is a mixture of aluminic and ferric hydrates, and was first found in the district Baux, near Arles, in Provence. It was discovered later on in other parts of the South of France. It also occurs in the Departments Var and Bouches du Rhône over a length of 95 miles in beds of a thickness amounting in places to between 65 feet and 95 feet.<sup>1</sup> Beds have also been found in Carniola, Nassau-Hesse, Ireland, Lecchi and Calabria, Senegal, Georgia, Alabama, Arkansas, California, Florida, and New South Wales. There are two kinds of bauxite, the red and the white, containing little and much silica respectively. The former is preferred as a source of aluminium.

The composition of various kinds of French bauxite may be seen in the following analyses:<sup>2</sup> No. I. is from Villeveyrac (Hérault), II. from Nas de Gilles at Baux, III. from Paradon at Baux, IV. is a silicated bauxite at Villeveyrac, V. a silicated bauxite from Baux.

	I.	II.	III.	IV.	V.
Alumina . . . . .	78·10	57·6	—	43·20	58·1
Alumina with titanac acid . .	—	—	18	—	—
Ferric oxide . . . . .	1·02	25·3	60	7·25	3·8
Silica . . . . .	5·78	5·9	4	34·40	24·9
Water . . . . .	15·10	—	—	15·15	14·2
Water and calcium carbonate.	—	11·2	18	—	—

The following is the composition of a German bauxite from Mühlbach, near Hadamar, in Nassau-Hesse:—

Alumina . . . . .	55·610
Ferric oxide . . . . .	7·170
Silica . . . . .	4·417
Chalk . . . . .	0·386
Magnesia . . . . .	trace
Water and loss by ignition . . .	32·330

The following are three specimens of a variety called wochenite from Feistritz, in Carniola, analysed by G. Schnitzer:—

	Brown Wochenite.	Yellow Wochenite.	White Wochenite.
Alumina . . . . .	44·4	54·1	64·6
Ferric oxide . . . . .	30·3	10·4	2·0
Silica . . . . .	25·0	12·0	7·5
Water and loss by ignition	9·7	21·9	24·7

<sup>1</sup> *Revue Univ. des Mines*, 1863, xiv., 387

<sup>2</sup> Knab, *Métallurgie*, p. 581.

The analyses of two other specimens of bauxite may be given here<sup>1</sup>:—

	Bauxite from Lecchi né Marsi, Italy.	Red ore from Emmaville, N.S. Wales.
Alumina . . . . .	47·44 to 57·00	42·20
Ferric oxide . . . . .	25·98 „ 36·77	28·91
Silica . . . . .	2·33 „ 4·06	0·16
Titanium oxide . . . . .	1·17 „ 2·86	4·75
Water and volatile . . . . .	The remainder.	23·45
Lime . . . . .	—	0·28
Magnesium . . . . .	—	0·37
Potassium and sodium carbonates	—	0·17

Most bauxite is at present supplied from France, Ireland and the States (Alabama and Georgia).

Bauxite is first converted into alumina, which is the true material from which the metal is extracted.

*Cryolite*, a double fluoride of sodium and aluminium of the formula  $\text{Al}_2\text{F}_6 + 6\text{NaF}$ , occurs at Ivittut in the Bay of Arsuk in South Greenland, where it forms an extensive deposit. At the surface it is white, at 10 feet deep it is blue-green, at 15 feet it is black, and transparent at the edges. The darker kinds become white when ignited.

The composition of pure cryolite is as follows:—

Aluminium . . . . .	13·07 per cent.
Sodium . . . . .	33·35 „
Fluorine . . . . .	53·58 „

Cryolite can be worked up directly into the metal, or first converted into the oxide.

Alum can be obtained from certain rocks and minerals containing aluminium sulphate; it is used as a source of alumina, and from the latter the metal is obtained. Such minerals are *alum-earth*, *alum-shale*, *alum-stone* or *alunite*, *hair-salt* or *alunogen*, *aluminite*. *Corundum*, which forms rubies and sapphires when in its purest forms, could only be used as an ore for aluminium in its impure form, in which it is known as emery. This is found at Naxos in Greece, and at Chester in Massachusetts, and has recently been discovered in large quantities in the States of North Carolina and Georgia. At present it is used as a precious stone and as an abrasive; it is also prepared artificially from bauxite.<sup>2</sup>

#### THE EXTRACTION OF ALUMINIUM.

Aluminium can be obtained in the dry way and by electro-metal-lurgical methods. Its extraction in the wet way, as a deposit from

<sup>1</sup> *The Min. Ind.*, 1902, p. 14.

<sup>2</sup> *Ibid.*, p. 16.

aqueous solution, has hitherto been found impossible, as no metal has been found to precipitate it; neither has its deposition from such solution by an electric current been found possible. At present it is prepared exclusively by the electrolysis of dry aluminium compounds, so that we may distinguish for descriptive purposes:

- I. The extraction of aluminium in the dry way.
- II. The extraction of aluminium electro-metallurgically.

### I. EXTRACTION OF ALUMINIUM IN THE DRY WAY.

The most important dry methods which have been proposed for the extraction of aluminium depend firstly upon the precipitation of the metal from its molten halides, and secondly upon the reduction of alumina by carbon. Numerous other proposals have not been tried, being foredoomed to failure, or have not passed the experimental stage, so that we need not dwell upon them here.

#### A.—THE EXTRACTION OF ALUMINIUM BY PRECIPITATION OF THE METAL WITH MAGNESIUM OR SODIUM FROM ITS FUSED HALIDE.

Since this method is no longer practised, it will only be necessary to pass the various processes in short review, although they are very important in the metallurgical history of aluminium, and formed for a long time the chief branch of the industry. They are all based on the decomposition of fused halides of the metal by sodium or magnesium, as already mentioned. The oldest process in which aluminium and sodium chloride were used, was invented by Deville and improved by Castner.

In certain works cryolite is used instead of this double chloride, as in Netto's process, and finally Grabau suggested aluminium fluoride.

#### *Devil's Process.*

This was based on the experiments of Wöhler, who had obtained aluminium in 1827 by decomposing its chloride by potassium. In 1854 Deville substituted the much more suitable double chloride, replaced potassium by less costly sodium, and so made the production of the metal possible on a large scale.

The process consisted in heating the double chloride, mixed with cryolite as a flux, with sodium in a reverberatory furnace at a gradually increasing temperature, when aluminium and sodium chloride were formed.

At the Salindres Aluminium Works (Gard), the largest in France, bauxite was the source of the double chloride of aluminium and sodium. It had to be first converted into aluminium hydrate, which was heated alone to  $150^{\circ}\text{C}$ ., and then converted into the double chloride by ignition with salt and carbon in a stream of chlorine gas.

The production of the pure hydrate from bauxite was effected by fusing it with soda to form sodium aluminate, lixiviating this compound with water, and treating the solution with carbon dioxide, which threw down aluminium hydrate. For this purpose bauxite was powdered and intimately mixed with soda, and the mixture fused in a reverberatory furnace of the Leblanc-soda pattern. (A charge consisted of  $9\frac{1}{2}$  cwt. of bauxite and 6 cwt. of soda, and was heated five or six hours.) Thus the alumina became converted into sodium aluminate, while the iron oxide was unattacked.

The aluminate was washed out by water in cylindrical vessels of iron plate, with double bottoms and linen filters. The liquid was transferred to special vessels, each holding 264 gallons, and there treated with carbon dioxide obtained from chalk and hydrochloric acid. Sodium carbonate was formed and remained in solution, while hydrate of alumina was precipitated. The vessels were provided with agitators, and had double bottoms, through which steam was led during the precipitation for five or six hours: the temperature was kept up to  $70^{\circ}\text{C}$ .

The precipitate and the solution were brought into a special vessel, in which the former subsided and the liquid was poured off. The hydrate was ready to be converted into chloride after repeated washings. It then contained 47.5 per cent. of alumina, 50 per cent. of water, and 2.5 per cent. of sodium carbonate.

The solution of sodium carbonate separated from the precipitate was evaporated down and used again to convert bauxite into sodium aluminate.

The hydrate of aluminium was next mixed with sodium chloride and finely-powdered wood charcoal, and the mixture made into balls the size of the fist, with a little water, and dried at  $150^{\circ}\text{C}$ . The dried balls were placed in a vertical retort of fireclay, and heated to a white heat in a current of chlorine. The volatile double chloride of sodium and aluminium was thus produced, and was collected in condensing chambers attached to the retort, while the carbon monoxide formed, and the excess of chlorine, passed off through a chimney.

The arrangement of the apparatus can be seen in Fig. 496. *R* is the retort, *F* the grate, *P* the fire-bridge; *n, n*, are the flues, *O* is the

opening to admit chlorine, which enters the retort by a porcelain tube; *L* is the condensing chamber for the double chloride, furnished with a movable cover *M*. Sometimes large earthen pots were used instead of this chamber, with covers well luted down. The incondensable vapours were led through a tube in the cover into chimney flues. The balls were placed in the retort through the opening *Z*, closed by a cover. The residue after firing was removed by an opening *V* in the bottom of the retort, closed by a brick slab, forced upwards by means of a screw.

After the balls had been put into the retort, heat was applied to remove water from the aluminium hydrate; after it had passed off,

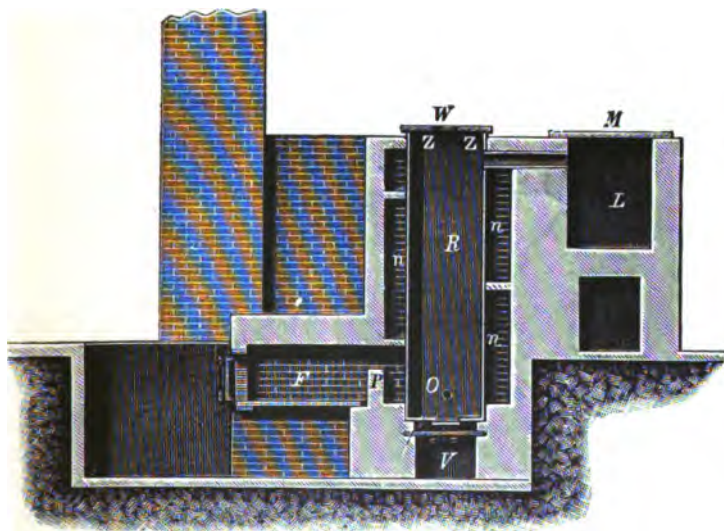
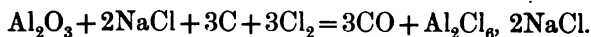


FIG. 496.

chlorine was led through and the temperature raised gradually to a white heat. Chlorine was absorbed during the whole operation, and the double chloride appeared in the condensing chamber as a crystalline mass with a yellow colour (due to ferric and ferrous chlorides). The reaction is shown in the following equation—



One distillation lasted 12 hours. Towards the close the absorption of chlorine became irregular.

The separation of aluminium from the double chloride took place with the assistance of cryolite as a flux. This was necessary to aid the small portions of separated metal to run together. The mixture

consisted of 220 lbs. of the chloride, 100 lbs. of cryolite, 77 lbs. of sodium. The first two were in the form of powder, the sodium in pieces about  $\frac{1}{16}$  to  $\frac{1}{8}$  of a cubic inch. The mass, divided into four portions, was charged into a reverberatory furnace with a well and sloping bed at a low red heat. The heat was regularly increased for three hours, after which the separation was complete, and the tapping was proceeded with. First, the slag was run into iron waggons, then the aluminium into heated cast-iron ladles, and, lastly, a mixture of sodium chloride and cryolite containing small portions of aluminium was tapped into another cast-iron ladle. To cast it into bars the aluminium was poured into small cast-iron moulds; the grains of aluminium separated out from the mixture tapped last.

The sodium was produced by heating a mixture of sodium carbonate, coal and calcium carbonate in iron tubes.

In 1882 the cost of production of aluminium by this process was about thirty shillings a pound (80 fr. per kg.).<sup>1</sup> The market price in Berlin in 1885 was about £2 18s. per pound (130 m. per kg.). At present it is made by the electric process at less than one shilling a pound (2 m. per kg.).

#### *The Process of Deville and Castner.*

This is the Deville process improved by J. Castner. The improvements consist in a cheaper production of alumina and of sodium, in making chlorine by the Weldon process, in producing the double chloride free from iron, and in using plant of greater capacity to make and to reduce the chloride. The process was carried out at Oldbury, near Birmingham, and brought down the cost of production to about twenty shillings per pound (44s. per kg.). It has also been replaced by the electrical method, and has gone out of use.

The alumina was made from alum by Webster's process.<sup>2</sup> The alum was mixed with tar and ignited. The mass, after ignition, was treated with hydrochloric acid to decompose any sulphides produced. then mixed with powdered wood charcoal and ignited in a retort in a current of steam and air. After this ignition the mass was lixiviated with water, potassium sulphate went into solution, and alumina remained behind.

The double chloride was made in clay retorts 10 feet long, five of which were enclosed in a reverberatory gas-fired furnace of the regenerative type; the process was similar to Deville's. Chlorine was made by Weldon's process in a neighbouring works, and led in to a

<sup>1</sup> Würz, *Wagner's Jahresbericht*, 1882, 122.

<sup>2</sup> *Wagner's Jahresbericht*, 1883, p. 153.

gasometer by earthenware pipes; it passed from this at constant pressure into the retort. Castner had a process, kept secret, for removing the chlorides of iron down to 0.01 per cent. from the double chloride, whereas originally its admixture gave the substance a pale yellow, or even dark red, colour, and caused the aluminium produced to contain as much as 5 per cent. of iron.

In Castner's process<sup>1</sup> sodium was made from caustic soda and carbide of iron, which latter was produced by heating ferric oxide with pitch (70 parts iron to 30 of carbon). According to Roscoe the iron of this compound does not enter into the reaction, which takes place in accordance with the equation:—



The great advantage of this method for obtaining sodium is that the caustic soda is kept in the fused state by the reaction, which is not the case when ordinary soda is used. Further, if soda-ash is used, vessels of very small diameter must be employed to keep up the temperature necessary for reduction. In Castner's process egg-shaped steel vessels, 2 feet long, and  $1\frac{1}{2}$  feet in greatest diameter, were used for the decomposition; they held 80 lb. charges. The covers of these were fixed, while the vessels themselves, which stood on a movable plate closing the furnace bottom, could be forced upwards to the covers by hydraulic pressure, making an air-tight joint.

The vapours of sodium were led through a tube in the cover of each vessel into a special inclined cylindrical condenser,  $3\frac{1}{2}$  feet long and 5 inches in diameter. The condensed sodium flowed through an opening three-quarters way down this condenser into a vessel filled to a certain height with petroleum, in which it solidified. The incondensable gases passed out at an opening at the end of the cylinder. The distillation lasted 1 or 2 hours. During this time about 7 lbs. of sodium collected in the receptacle. From 560 lbs. of soda, 67 lbs. of sodium and 540 lbs. of sodium carbonate were obtained; the latter was reconverted into caustic soda by lime.

The decomposition of aluminium-sodium chloride by sodium was carried on in gas-fired reverberatory furnaces with sloping hearths 6 feet square. To 11 cwts. of double chloride  $5\frac{1}{2}$  cwts. of cryolite were added, and then 350 lbs. of sodium cut into slices by a machine; the whole was then intimately mixed in drums. From this charge a little more than 1 cwt. of 99 per cent. aluminium was obtained; the impurities were a few tenths per cent. of silicon and iron.

<sup>1</sup> Ger. Pat., No. 40415.

*Netto's Process.*

This produces metallic aluminium by decomposing cryolite with sodium; the latter is obtained by reducing caustic soda with coal. It used to be practised at Wallsend, near Newcastle-on-Tyne, but has been given up.

About 200 lbs. of cryolite and 100 of salt were fused together for  $1\frac{1}{2}$  hours in a reverberatory furnace, and the fused mass transferred to a converter, previously warmed. Then sodium, in lumps of about  $5\frac{1}{2}$  lbs. weight, was pressed down to the bottom of the converter, by two workmen, with a plunger, until about 44 lbs. of sodium had been put in. The sodium decomposed the cryolite, setting aluminium free and forming sodium fluoride, which passed for the most part into the slag, a small quantity being given off as white fumes. During the action the mass, which was syrupy to begin with, became quite liquid, and aluminium collected at the bottom of the converter.

Although the specific gravity of solid cryolite is 3, and that of solid aluminium only 2·7, molten aluminium, nevertheless, sinks in molten cryolite, because cryolite expands very considerably in melting, and so becomes lighter, whereas aluminium expands very little.

The slag was poured into a special iron vessel, and then the aluminium into another, also of iron, in which it solidified. From 40 lbs. of sodium, 10 lbs. of aluminium were obtained. The slag contained 40 per cent. of sodium fluoride, 43 per cent. of sodium chloride, 15 per cent. of cryolite, 0·75 per cent. of metallic aluminium and a small quantity of alumina. If a metal free from iron and silicon was desired, the sodium added was only one-third of that necessary to decompose the cryolite. Then iron and silicon were reduced at the same time as aluminium and taken up by the metal. The fused mass was separated from these metals by pouring it into a second converter, where metal with 98 to 99 per cent. of aluminium was obtained by the further addition of sodium.

The 0·75 per cent. of the metal in the slag was removed by copper, and formed aluminium bronze. The slag was then worked up into cryolite and Glauber's salt, by the addition of aluminium sulphate.

The following reaction took place:—



The sodium sulphate was washed out of the fused mass, and cryolite remained as residue.

To make the sodium, Netto allowed fused caustic soda to drop on a layer of red-hot coke which was at the bottom of an upright



cylindrical retort of cast-iron or cast-steel, covered by a jacket of clay. Part of the soda was reduced to sodium in the state of vapour, the remainder forming sodium carbonate. The vapours of sodium were condensed in receivers attached to the upper part of the retort, and collected in a vessel containing oil. The sodium carbonate in a fluid state collected at the bottom of the retort and was tapped off from time to time. To produce 1 lb. of sodium and 9 lbs. of soda slag containing 60 per cent. carbonate, 6 lbs. of caustic soda, 12 of coke, and  $1\frac{1}{2}$  of wood charcoal were required, the retort consumption being equal to 1.2 lbs. of cast-iron.

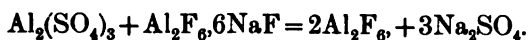
This process of Netto, although carefully thought out, cannot possibly compete with the electrolytic method.

#### *Grabau's Process.*<sup>1</sup>

This consists in decomposing aluminium fluoride ( $\text{Al}_2\text{F}_6$ ) with sodium according to the equation:—



Thus besides the metal an artificial cryolite is obtained which is used to make aluminium fluoride. This is made by heating aluminium sulphate and cryolite, thus:



After drying and igniting the whole, the sodium sulphate is washed out and the residue of aluminium fluoride is ready for the metallurgical process.

The arrangements for carrying out this process are to be seen in Figs. 497 and 498.<sup>2</sup>  $x$  and  $y$  are vessels for the heating of the substances used. They are made of cast-iron and lined with fire-clay. In  $x$  the aluminium fluoride is warmed, in  $y$  the sodium is melted.  $x$  is closed by a sliding piece  $v$  at its lower end,  $y$  has a stopcock  $t$ .  $R$  is the fire-place,  $Z, Z$ , are the flues,  $W$  the lower part of the chimney.  $M$  is the vessel for the reduction, hung on trunnions. It is formed of hollow iron walls cooled by water which passes in and out by the tubes  $g, g$ .  $N$  is the vessel which receives the molten mass after the action, and is likewise jacketed with water which flows in and out at  $g', g'$ .

When the process is started  $x$  is filled with aluminium fluoride

<sup>1</sup> Ger. Pats., Nos. 47031, 48535, 51898.

<sup>2</sup> Dammer, *Chem. Technologie*. Vol. ii. (*Métallurgie*), p. 217.

(or cryolite if it is an initial process) and  $y$  with sodium. When the fluoride is red-hot (which is known by its giving off white fumes), the sodium is tapped into the vessel  $M$  by turning the stop-cock  $t$ . Then the slide  $v$  is drawn out and the powdered fluoride falls also into the vessel, where it collects upon and covers the molten sodium. The action which at once begins, disengages so much heat that the fluoride is melted. The length of time needed is only some

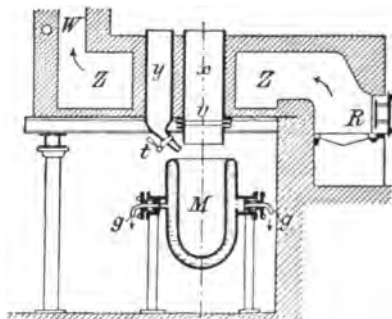


FIG. 497.

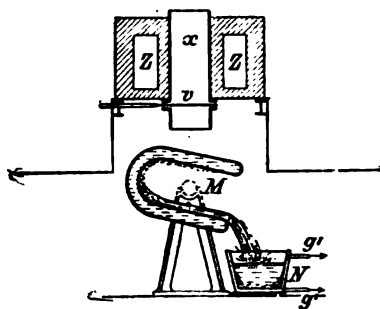


FIG. 498.

seconds. Aluminium collects at the bottom of the pot. This is tipped up and its fluid contents emptied into the receiver  $N$ .

In this method more than 90 per cent. of the sodium is made use of. It is made electrolytically from common salt, and chlorine obtained as a by-product.<sup>1</sup>

The process has not been an economic success, in spite of the fact that it is well thought out, and is the best of all those for which sodium is necessary, on account of the low cost of production of that metal.

Beketoff<sup>2</sup> used magnesium instead of sodium for the extraction of aluminium from cryolite. This process was carried on for some time in certain works, *e.g.* in Hemelingen, but has been abandoned.

## B. THE EXTRACTION OF ALUMINIUM BY REDUCTION OF ALUMINA.

The alumina is reduced to metal by carbon at a temperature so high that the electric current must be used. This method was first proposed by Monkton<sup>3</sup> in 1862, at a time when dynamos had not been invented and when electrical energy was not cheaply obtained. The reductibility of alumina by carbon has often been questioned.

<sup>1</sup> Ger. Pat., October 8, 1889, No. 51898.

<sup>2</sup> *Jahresbericht der Chemie*, 1865.

<sup>3</sup> Eng. Pat., 1862, No. 264.

Borchers<sup>1</sup> has obtained proof that the alumina is reduced to metal by the electrically heated carbon by means of a simple experiment, which is described below.

A thin carbon pencil *W* (Fig. 499) of about one-eighth of an inch in diameter and two inches long, is made fast between two strong sticks of carbon *K* one inch or one and a quarter inch in diameter. This pencil passes lengthwise through a small cylindrical paper shell *P*, filled with an intimate mixture *M* of alumina and charcoal (obtained by repeated mixing and igniting aluminium hydrate and tar). Two small cork discs close the ends of the cartridge. After the latter is well covered by coarsely-powdered wood charcoal, the whole arrangement is put into a circuit in which a current of 35 to 40 amperes is passing, and remains there two or three minutes.

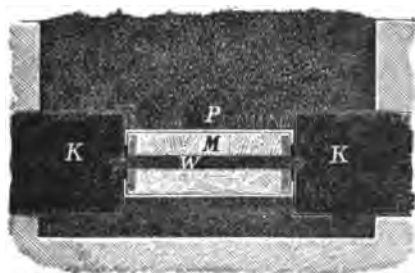


FIG. 499.

The cartridge thus heated is then cooled to a convenient temperature, and when the charcoal powder has been removed the central pencil is found to be covered with a sintered mass, which consists of aluminium strongly impregnated with carbon. The absolute impossibility that a spark should be produced in this experiment will be quite obvious, and there can be no possibility of electrolytic decomposition as long as there is no break in the current within the mixture. It need hardly be mentioned that if copper or copper oxide be added to the mixture aluminium bronze will be produced. With this simple arrangement it is an easy matter to show by experiment that every metallic oxide is reduced by carbon at a sufficiently high temperature.<sup>2</sup>

To obtain the temperature needful for reduction, Borchers passed a current of 35 to 40 amperes through his carbon pencil ( $\frac{1}{8}$  of an inch in diameter), so that the current density was from 5 to 6 amperes per square millimetre. Borchers maintains that twice that

<sup>1</sup> *Elektrometallurgie*, p. 97.

<sup>2</sup> *Ibid.*, p. 102.

density will suffice in the most obstinate cases. The E.M.F. requisite for the passage of 1 ampere through a carbon pencil 1 mm. long is 0.3 to 0.4 volt, the current density being 6 to 10 amperes per square millimetre.

It is not possible however to obtain aluminium suitable for technical use by the reduction of alumina with carbon, since aluminium carbide,  $C_3Al_4$ , is the chief product of that reaction (Moissan). Hence the preparation of aluminium in this way has never attained any practical importance, despite numerous endeavours. The method however has been used for the production of aluminium alloys.

The brothers Cowles in 1884 were the first to prepare these alloys on a large scale after they had failed in attempting the extraction of aluminium itself. Their method consisted in heating in their electric furnace a mixture of alumina, carbon and the metal or the oxide of the metal needed in the alloy. The alumina was reduced by the electrically heated carbon and the aluminium then alloyed with the metal present. The latter was also reduced from its oxide in case that had been added. Further description of this process and the furnace used will be found under the head, "The Production of Aluminium Alloys."

## 2. THE ELECTROMETALLURGICAL PRODUCTION OF ALUMINIUM.

This has not been possible hitherto with aqueous solutions, very small quantities of metal being obtained in this way. None of the many proposals made in Borchers' *Elektrometallurgie*, p. 104, has come into use.

In the present state of technological knowledge, aluminium must be obtained by electrolysing fused compounds. Of such compounds, alumina, halides of aluminium and aluminium sulphide have thus far received consideration; and definite use has been made only of solutions of alumina in molten halides of the alkali metals, of the alkali earths and of aluminium itself. In these operations the heat required to melt and to keep the materials in the molten condition is supplied by the current itself. The cost of production of aluminium in this way has been so much reduced, that methods founded upon the decomposition of aluminium halides with sodium and magnesium have not been able to compete successfully and have thus gone out of use. The first experiment of the kind was made by Bunsen and Deville in 1854.

Bunsen decomposed aluminium-sodium chloride fused at  $200^{\circ}\text{C}$ . in a porcelain crucible. This was divided into two parts by a porcelain partition extending nearly to the bottom, and each part contained a carbon electrode. The carbon plate forming the anode was plain, but that forming the cathode was concave and had horizontal saw-like depressions in which the molten metal collected. At a low temperature aluminium separated as powder. To avoid this undesirable result the temperature was raised to that of the melting point of silver, and common salt was introduced into the crucible.

Buttons of aluminium were then obtained in these depressions, and they were put into strongly heated molten salt, where they united.

Deville decomposed the double chloride of aluminium and sodium similarly, using however a platinum cathode instead of carbon. His apparatus is shown in Fig. 500.<sup>1</sup>

*H* is a Hessian crucible in which is placed a porcelain one *P*. *D* is the cover, through which passes the cathode *K*, a strip of platinum. The cover is also pierced by a porous clay cell *R*, which contains the anode *A*, a piece of gas-coke, hanging in it. The crucible and the porous cell were filled to the same level with the fused double chloride, and then the current was passed. Aluminium mixed with salt formed a deposit on the cathode, and was removed from time to time by lifting the strip of platinum out of the crucible. The mixture of metal and salt was remelted, and a button obtained.

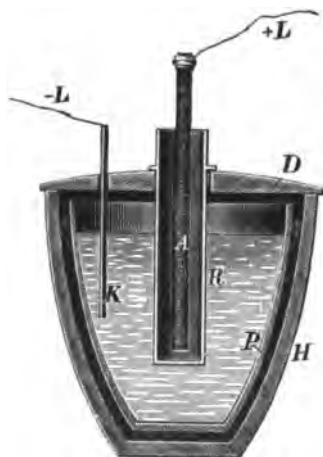


FIG. 500.

Attempts to manufacture aluminium upon these lines were beset by insuperable obstacles. No material could be found suitable for making vessels for fusing and electrolysing, for when the vessels were heated from the outside, all that were tried were acted on by the fused haloid salts, or by the metal itself, at the high temperature, and impure aluminium resulted. Crucibles of siliceous material caused silicon to pass into the aluminium. Clay and graphite were attacked by the double chloride. Compressed coke crucibles were so porous that they could not be heated unless surrounded by thick jackets. Metal vessels could not stand the temperature, they were

<sup>1</sup> Borchers, *Elektrometallurgie*, p. 114.

attacked by their molten contents and thus alloyed with the aluminium.

The one thing to be done to make the process possible was to generate the heat within the vessels, by means of an electric current. When this was done the production of aluminium on a large scale became possible.

The production of heat by the current itself may be effected by allowing an electric arc to be formed within the containing vessels, or by placing the materials to be fused and decomposed as resisting media in the circuit. The latter method has proved far more profitable than producing an electric arc. This, even when weak, has a far higher temperature than is necessary to fuse and keep liquid aluminium compounds, so that a great part of the heat produced is wasted. Further, its effect is concentrated into so small a space that it becomes difficult to heat a large quantity of the aluminium compound at all evenly.

These objections do not apply to the generation of heat by the resistance of aluminium compounds in the circuit. The heat developed by the resistance of these in the fused condition is great enough to fuse, and keep liquid, substances of high melting point if a suitable current is employed. Moreover the electrolyte will become heated uniformly, even though the electrodes dipping into the fused material possess a smaller area than the section of the cell. This second method of heating is consequently chiefly employed at present.

It was first suggested by Bradley in 1883.<sup>1</sup>

It was first applied to the production of alloys of aluminium from its fused compounds, and so used by the brothers Cowles as early as 1884, and in 1886 by Héroult.

The brothers Cowles led the current through a mixture of alumina and coal, while Héroult melted alumina alone and electrolysed it without coal. In both cases aluminium was separated and alloyed with copper.

The action of the current in Cowles' process was mainly electrothermal, in Héroult's process it was first electrothermal and then electrolytic.

The original furnace of Héroult, as used for the preparation of aluminium alloys at Neuhausen, in Switzerland, is also suitable for the preparation of aluminium. Its arrangement is shown in Figs. 501, 502.<sup>2</sup>

<sup>1</sup> U.S. Pat., December 8, 1891, No. 464933.

<sup>2</sup> *Schweizer Bauzeitung*, 1888, 28.

The vessel in which the fusion and decomposition take place is a cast-iron box *a* which is provided with a strong lining of carbon plates *A*. These are cemented together by tar, syrup or l  vulose. To bring this lining into contact as close as possible with the iron, the latter is cast round it. When cooled the metal firmly adheres to the lining. The box itself is made the negative terminal by the copper rod *a*<sub>1</sub>. The positive terminal consists of a series of carbon plates

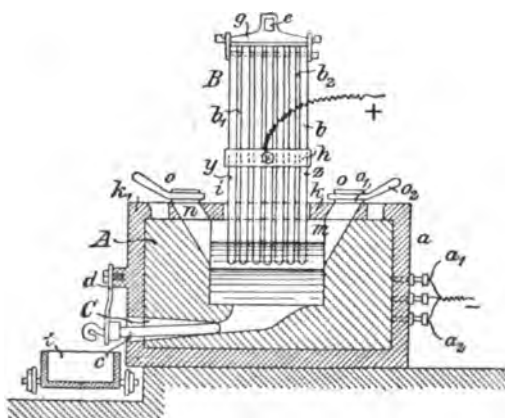


FIG. 501.

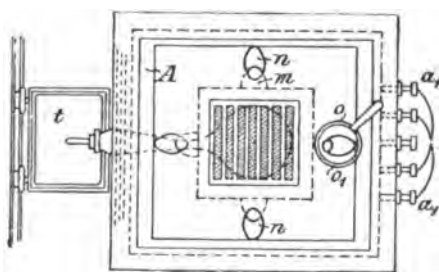


FIG. 502.

*b, b*<sub>1</sub>, *b*<sub>2</sub>, etc., which dip into the vessel. These plates are either firmly attached to each other, or the spaces left between them are filled with a conducting body, copper or soft coal. At the upper end they are held together by the framework *g*, at the middle by the framework *h*. The former has an eye *e* to which a chain can be fastened and by which the electrode can be put into position and raised and lowered at will. The current is led to the framework *h*.

The box is closed at the top by graphite plates, in which are various openings, *i, n, m*; *i* is the space to admit the anode, *n* and

*m* are openings for charging and to let out gases. These have plates for covers (*o* and *o*<sub>1</sub>) provided with handles. The space between the upper edges of the box and the graphite top is filled with powdered wood charcoal. A taphole *c* enters the box at the deepest part of the bottom, and through this the aluminium alloy is tapped into the mould *t*, lined with charcoal, which produces the alloy in the form of a rectangular block. The taphole *c* is closed with a stick of charcoal *e* provided with a handle *d*.

The working is as follows: Finely divided copper is sprinkled on the bottom of the vessel, the anode is dropped in, the circuit closed, and the copper melted by the electric arc. The alumina is placed on top of this copper, which now acts as the cathode. The alumina melts, becomes a conductor, and is consequently split up by the current into aluminium and oxygen. The former passes into the copper and forms aluminium bronze, while oxygen goes to the anode and forms carbon monoxide with the carbon. This gas passes away through the openings. The alloy is tapped out from time to time, and the anode at the same time lifted out, while copper and alumina are added when necessary. The anode can be raised or lowered according to the resistance wanted.

The current used is 13,000 ampères working with a difference of potential of 12 to 15 volts.

Pure aluminium is at present extracted from solutions of alumina in wrought-iron baths strengthened by angle irons, the walls of the bath being coated with the solid electrolyte. This coating protects the iron from the corrosive action of the electrolyte, and is preferable to a carbon lining since the latter allows of the passage of the molten electrolyte through capillary pores, the result being that the bath is speedily destroyed. The bottom of the bath is covered with carbon plates which serve as cathodes until covered with aluminium, when the metal acts as such. The anodes are also of carbon. Although carbon-lined baths are still used, it is better in practice to restrict the use of that element to such places as, for instance, the bottom of the bath, where its presence is quite necessary.

Water-cooled metallic cathodes have been used, but their use on a large scale is now given up, since the metal is attacked by the electrolyte, and thus impurities are introduced into the bath. In addition, the carbon used as cathode conducts heat as well as metal and the air circulating under the bath promotes sufficient cooling, the temperature of the molten electrolyte not exceeding 750° C.

Since the carbon electrodes must not contain too much mineral



matter, or the electrolyte and the aluminium will become contaminated, they are made either of retort graphite with at most 1 per cent. of ash, or of petroleum coke with 0.5 per cent. of ash. The latter is the residue left on the distillation of petroleum. These materials are powdered, made into a plastic mass with soot, pitch or tar, or mixtures of these bodies, pressed into moulds, and then heated until the hydrocarbons are volatilised and driven off. A little alumina is added in making the plastic mass, so that the electrodes are not burnt away in the process. The composition of the mixture is, according to Winterler<sup>1</sup> :—

80	parts of retort graphite or petroleum coke
8	„ tar
4	„ pitch
3	„ soot
5	„ alumina.

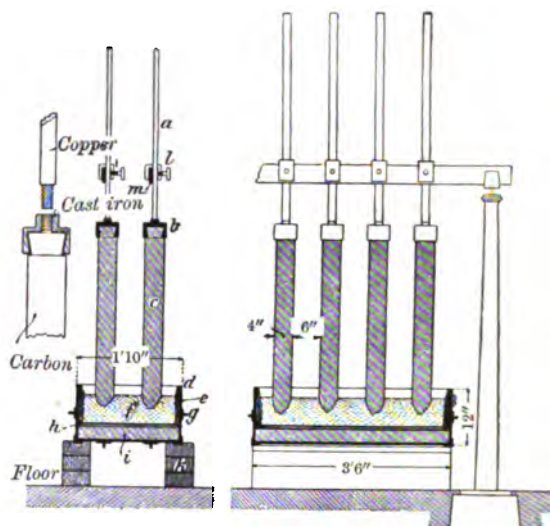
These electrodes are generally made at the aluminium works. The quantity of carbon consumed in the electrolytic process almost equals that of aluminium produced. Molten matter is withdrawn from the bath either by tapping or by ladling. The horizontal section of the melting area is 30 inches by 60 inches. According to Winterler (*op. cit.*) the best size of the bath for a current strength of 3,200 ampères is 41 inches long, 21 inches wide, and 12 inches high.

The construction of a modern bath used for working on a commercial scale is shown in Figs. 503 to 506,<sup>2</sup> where *d* is the bath of the above dimensions, *g* the stay pieces, *i* the cathode carbons, *c* the anodes held in the cast-iron clamps *b*, *a* the copper bars connected metallically with the copper leads *m* by the clamps *l*. The copper leads are on insulated supports, the cathode leads are screwed directly on to the iron baths. Air circulates under the bath and around the sides, and the cooling set up thereby causes a crust of the electrolyte to freeze on to the inner surface of the bath, thus preventing the corrosion of the iron by the molten electrolyte. *F* is the molten electrolyte, and *i* the aluminium coating upon the carbons.

The anodes are kept about  $2\frac{1}{2}$  inches apart from the cathodes, the distance being regulated every two hours under ordinary working conditions. The anodes are 6 inches from each other. If closer they are comparatively quickly destroyed, owing to the development of heat, if further away there is risk of the electrolyte freezing. At the larger works a number of such baths is kept running in series, reserve baths being arranged so that individual baths may be cut out for repairs

<sup>1</sup> *Die Aluminium Industrie*, Brunswick, 1903, p. 56.

<sup>2</sup> *Op. cit.*, p. 68.



FIGS. 503-505.

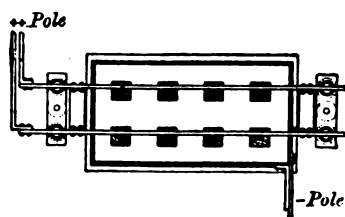


FIG. 506.

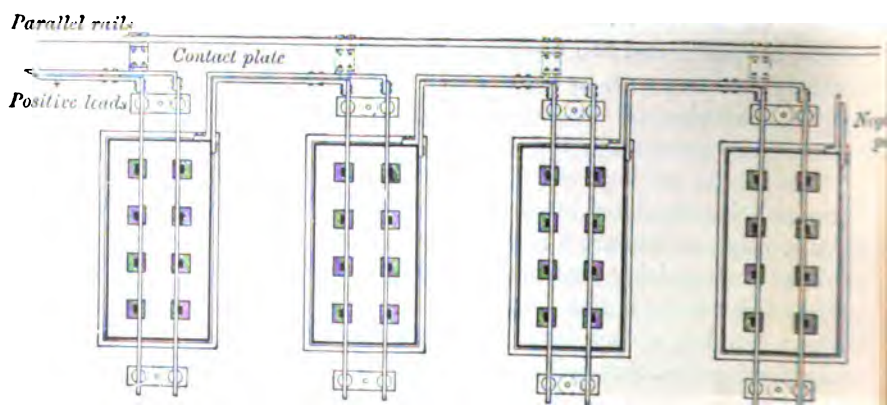


FIG. 507.

and cleaning, without disturbing the whole plant. An arrangement to effect this is shown in Fig. 507. The aluminium is ladled out every two days with an iron ladle.

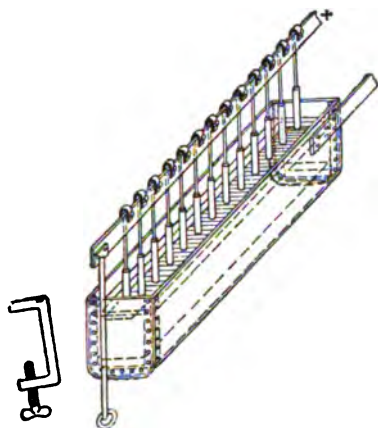


FIG. 508.

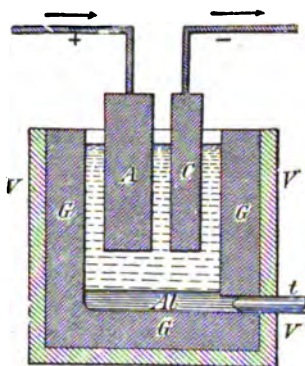


FIG. 510.

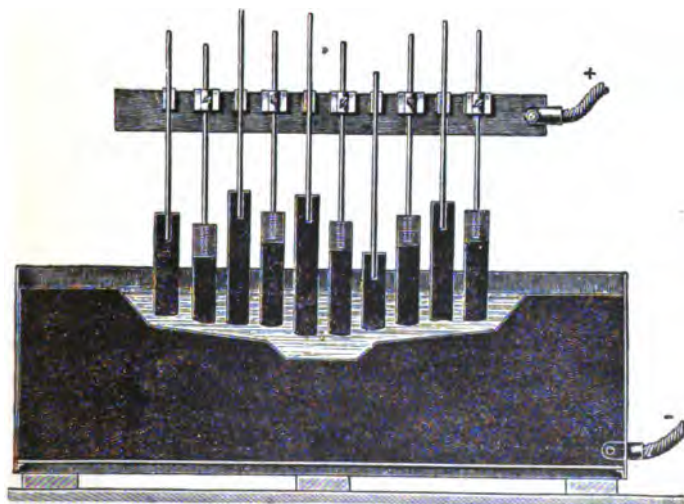


FIG. 509.

Hall's bath is used at the works of the Pittsburgh Reduction Co. This is represented in Fig. 508, and is an iron vessel lined with carbon. The carbon forms the cathode, and the anodes are carbon rods fastened to a copper rod. The anodes must be sunk deeper in the electrolyte from time to time. Richards' apparatus used at the same works is shown in Fig. 509.<sup>1</sup>

<sup>1</sup> *Aluminium*, J. R. Richards, 3rd ed., London, 1896.

Minet's apparatus is represented in Fig. 510.<sup>1</sup> It is a metal crucible lined with carbon, the metallic part *V* being hollow to allow of the circulation of air or water. *A* is the anode, *C* the cathode, and *t* the tapping channel. If the lining be thick enough and the cooling efficient, the temperature of the sides of the crucible can be brought below 500° C., so that the crucible may be made of aluminium. Nothing is known as to the practical use of this apparatus.

Fig. 511 shows a cylindrical carbon-lined bath which was formerly used at Neuhausen and at Froges. The cathode was a metal rod protruding through the lining, and the anodes were made of carbon rods bound together into plate form.

In 1891 Kiliani,<sup>2</sup> the former director of the *Aluminium-Industrie Co.*, patented the apparatus shown in Fig. 512. The anodes are revolvable; information is lacking about the nature of the cathodes and the lining. The bath *b* is supported on the columns *a*. The anode *e* is connected to the spindle *f*, and can be raised or lowered by turning the handle *h*<sup>2</sup>, which actuates the worm *hh*<sup>1</sup> and the spur-wheel *g*. The anode is revolved by means of the worm *i* and the spur-wheel *k* keyed on to the spindle. The current enters the spindle by a brush and thence passes to the anode, and leaves the bath through the rod *c*. The anode is kept in constant rotation during electrolysis.

Kiliani's successor, Schindler, patented in 1896 the bath shown in Figs. 513 to 517.<sup>3</sup> The anodes *A* are surrounded by metal jackets *B*, through which water circulates; *A*<sup>1</sup> are the cathodes, and *B*<sup>1</sup> the corresponding coolers. The current conduction is through these metal jackets. If the cathodes are not to be cooled, the plates *P*<sup>1</sup> form the leads.

An experimental apparatus of Borchers,<sup>4</sup> with which good results have been obtained, is shown in Fig. 518. *T* is the cylindrical electrolysing bath. This has iron sides and a clay bottom, and is lined (*F*) with alumina or some other difficultly fusible aluminium compound. The cathode *K* is a steel plate laid in the bottom of the bath, and protected from melting by the copper cooling tube *R* through which water passes. The water enters *R* through the pipe *E*, rises in the cooling tube, and escapes through the pipe *X*. The negative cable *N* is connected to *R* by the clamp *V*, and *R* is in metallic connection with the steel plate cathode. *A* is the carbon anode connected by an iron clamp with an iron rod which is bolted

<sup>1</sup> *Die Gewinnung des Aluminiums*, p. 63.

<sup>2</sup> Ger. Pat., 1891, No. 62851.

<sup>3</sup> U.S. Pat., 15 Dec., 1896, No. 573041.

<sup>4</sup> *Elektrometallurgie*, p. 143.

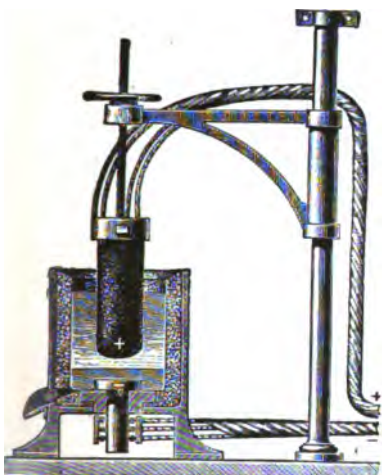


FIG. 511.

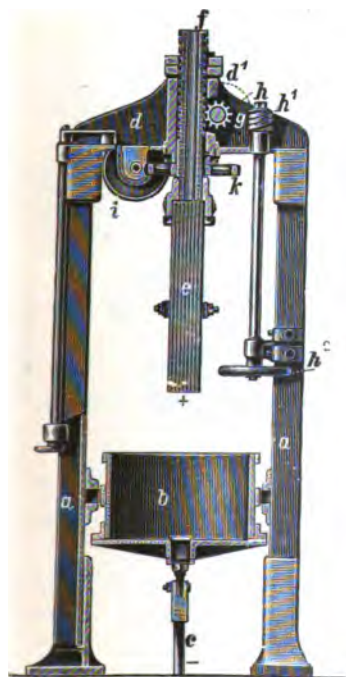
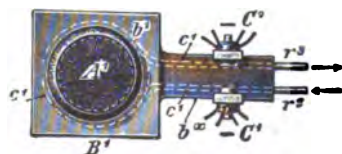
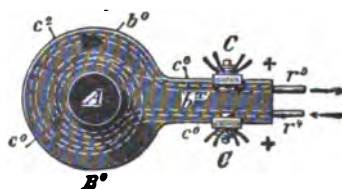
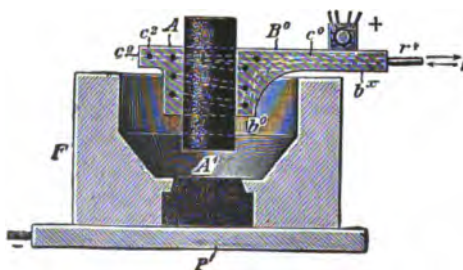
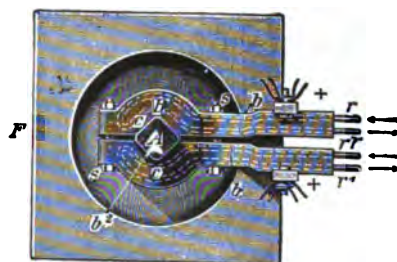
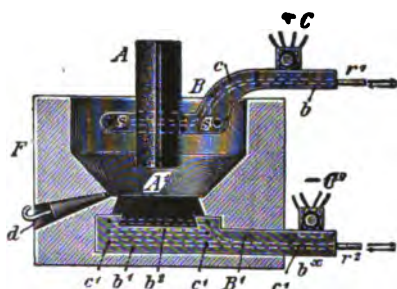


FIG. 512.



FIGS. 513—517.

tightly to the iron plate *U*. The current enters by the copper rod *P* which is in metallic connection with the above iron rod; the bath is insulated by the clay plate *J*. The aluminium is tapped at intervals at *S*, and run into the mould *G*, and the gases developed in the process escape through openings in the lid *D*. The lining is not attacked by reason of the cooling by air of the sides of the bath.

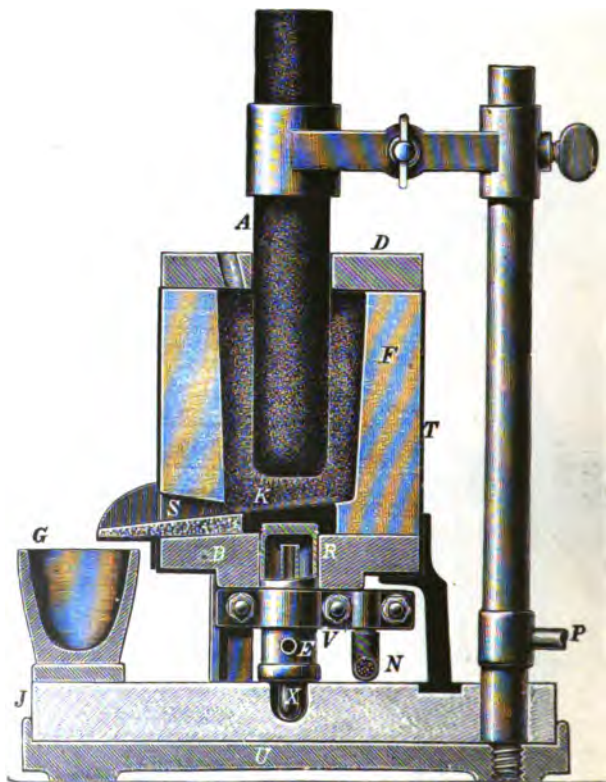


FIG. 518.

For constant working at high current densities, it is advisable to have water coolers either around the bath or in the lining.

To begin the operations a little aluminium is laid on the bottom of the bath and melted by bringing the anode near the cathode. The molten aluminium now forms the cathode. The electrolyte is then added; this melts and forms a liquid layer, separating cathode from anode. It is decomposed by the current into aluminium and oxygen, and fresh material is added in proportion as it is consumed.



Another experimental plant of Borchers<sup>1</sup> for use with higher current strengths is shown in Fig. 519. The cathode is made of coke and is cooled, the electrolyte is cryolite also cooled by surrounding it with a sheet copper jacket.

Mention may be made finally of the Kleiner-Fiertz bath<sup>2</sup> which is heated by the electric arc, and was constructed for the electrolysis of alumina dissolved in cryolite.

The construction is shown in Figs. 520 and 521.<sup>3</sup> *B* is the bath lined with bauxite or clay and filled with molten cryolite; *A* is the

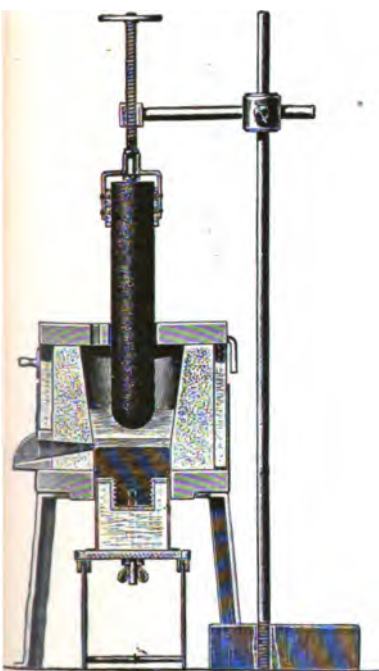


FIG. 519.

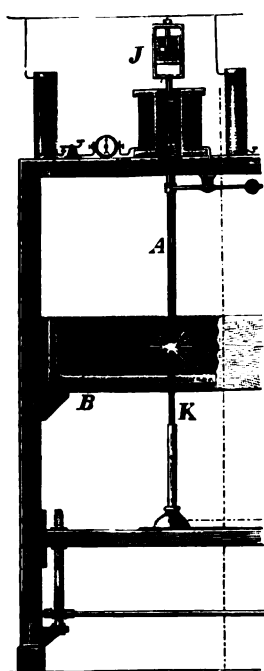


FIG. 520.



FIG. 521.

anode, *K* the cathode, both of which can be placed in any desired position. The movement of the anode is regulated by a weighted lever and a solenoid, the latter being connected with a piston dipping into water which governs its motion. On passing the current through, aluminium is liberated at the negative electrode, and the electrolyte is replenished by absorption of alumina from the lining. As stated above the electric arc is expensive, and restricted in action to its immediate neighbourhood. The molten materials readily form

<sup>1</sup> *Op. cit.*, p. 144.<sup>2</sup> Ger. Pat., 42,022.<sup>3</sup> Borchers, *op. cit.*, p. 124.

crusts with the cold matter around, so that continuous operation is only possible with extreme difficulty. This apparatus appears therefore not to have come into practical use.

We have now to consider the extraction of aluminium under three heads.

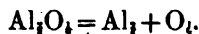
- A. By the electrolysis of alumina.
- B. By the electrolysis of aluminium fluoride.
- C. By the electrolysis of aluminium sulphide.

We may remark, however, that the details of processes and the economic results are kept secret, so that the author has been forced in the following account to restrict himself to the literature, patent and otherwise, which has been published on the subject.

A.—*The Production of Aluminium by Electrolysis of Alumina.*

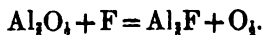
This method is the only one which has so far been used on a large scale. The alumina is dissolved in molten cryolite, and the loss of fluorine is made good by addition of aluminium fluoride. Haloid salts of the alkali metals and of the metals of the alkali earths have also been proposed as solvents in place of cryolite.

When cryolite is used as solvent, the alumina, melted by the heat of the current, dissolves in the cryolite, and becoming a conductor thereby is decomposed into aluminium and oxygen. The aluminium is liberated at the cathode, and the oxygen unites with the anode carbon, forming carbon monoxide. The decomposition may be represented thus:—



As the aluminium becomes exhausted, fresh alumina is added. Hérault, who, with the assistance of Kiliani, first made this method practicable on a large scale, and introduced it at Neuhausen in Switzerland,<sup>1</sup> furnished the proof that alumina is decomposed in the above way.<sup>2</sup> This view is now shared by most chemists.

Another view of the reaction maintained by Minet, is that the aluminium liberated at the cathode is the result of the decomposition of aluminium fluoride, the fluorine set free in this reaction attacking the alumina with liberation of oxygen and regeneration of aluminium fluoride, thus:—



The alumina and the cryolite must both be pure, in order that pure aluminium may be produced. The loss of fluorine during

<sup>1</sup> *Minet, op. cit.*, p. 68.

<sup>2</sup> *Ibid.*



electrolysis is best made good by addition of aluminium fluoride to the bath.

Pure alumina for the purposes of electrolysis is at present made from bauxite. It may also be prepared by treating white siliceous bauxite, kaolin, or pipe-clay with sulphuric acid, and by igniting the aluminium sulphate thus produced until all the sulphuric acid is driven off. It has been proposed to heat to whiteness bauxite containing but little silicon with sodium sulphate and coal. In this way sodium aluminate is formed, and this may be treated for alumina in the usual manner.

Bauxite is a hydrated aluminium sesquioxide, containing chiefly iron and silica as impurities. The alumina is extracted as sodium aluminate, from which pure aluminium hydroxide can be obtained and the latter on igniting leaves a residue of alumina. The older method of treatment was to heat the bauxite with soda in a reverberatory furnace until the mass sintered. This converted the iron into oxide, and the aluminium into sodium aluminate, and the latter could be separated from the silica and oxide of iron by solution in water. The alumina was precipitated from the solution as hydroxide by carbon dioxide, and the soda regenerated thereby was used again. After filtering, washing and drying the precipitate, it was heated to convert into it alumina.

In the newer method of Bayer sodium aluminate is prepared by the treatment of bauxite with soda solution under pressure, and the greater part of the alumina precipitated as hydroxide by stirring the solution with pure aluminium hydroxide. This process requires less expenditure on fuel, wages and repairs than the older process, and it has been introduced at a number of works.

The older process, or the smelting process, is carried out as follows: The bauxite is finely powdered in ball mills or disintegrators, mixed with calcined soda in the proportion of 3:1,<sup>1</sup> and heated to bright redness for two to three hours in a reverberatory furnace such as is used for the preparation of soda by the Leblanc process. The mixture does not melt properly on heating, but forms a soft crumbly mass, and the operation is over when a test taken from the furnace does not effervesce with acids. The mass is now lixiviated with warm water in sheet-iron vats as in Buff-Dunlop's process for the extraction of crude soda obtained in the Leblanc process. The solution of sodium aluminate thus obtained, of density 12° B., is either precipitated by carbon dioxide as in the older process, or it is stirred with aluminium hydroxide as in Bayer's process.

<sup>1</sup> Winteler, *Die Aluminium Industrie*, p. 25.

Precipitation with carbon dioxide is performed at 70° C in sheet-iron vessels of about 250 gallons capacity, the gas being derived either from the waste gases of the reverberatories or by burning limestone. It is scrubbed before using. The soda liquors are decanted from the precipitate to the precipitating vats and evaporated to recover the soda; the precipitate is washed, dried and ignited in a muffle or reverberatory furnace.

The most suitable furnace for this purpose is the sloping rotating cylinder, built by Fellner and Ziegler of Frankfort. This is shown in Figs. 522 and 523. The aluminium hydroxide is charged in at the upper end of the sheet-iron cylinder, lined with fire brick, and is

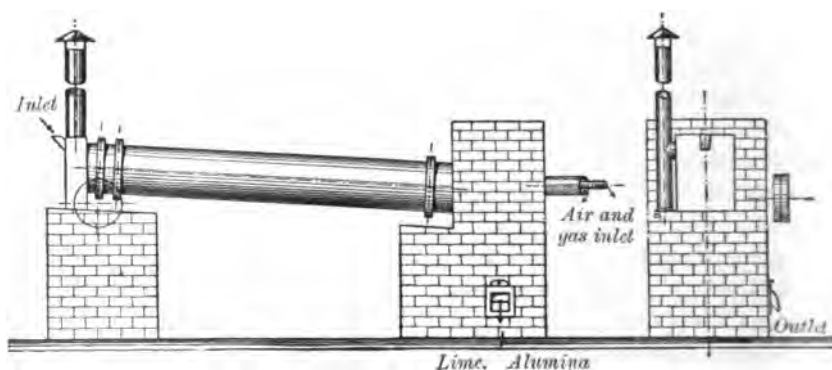


FIG. 522.

FIG. 523.

withdrawn as alumina through a door in the brickwork of the furnace at the lower end. Producer gas is used as fuel. This passes into the furnace through a pipe at the lower end of the same, and the air necessary for combustion is led in through a pipe which surrounds the gas pipe. The products of combustion and the water given up by the aluminium compound escape at the upper end of the cylinder into a flue, whence they pass to the stack.

Winteler<sup>1</sup> gives the following working results:—A mixture of bauxite and calcined soda in the proportion of 3:1 gave a soluble part containing 28·17 per cent. of  $\text{Al}_2\text{O}_3$  and 0·24 per cent. of silica. The residue contained:—

$\text{SiO}_2$	2·64	per cent.
$\text{Al}_2\text{O}_3$	3·73	„
$\text{Fe}_2\text{O}_3$	23·12	„
$\text{CaO}$	1·74	„
$\text{MgO}$	0·7	„

<sup>1</sup> *Op. cit.*, p. 28.

One hundred parts of alumina were obtained by igniting 175 parts of the hydroxide

*Bayer's process* consists in heating bauxite under pressure with strong alkali lye. It is in use at Larne Harbour in Ireland; the bauxite comes from County Antrim, and contains:—

$\text{Al}_2\text{O}_3$	. . . . .	56	per cent.
$\text{Fe}_2\text{O}_3$	. . . . .	3	„
$\text{SiO}_2$	. . . . .	12	„
$\text{TiO}_2$	. . . . .	3	„
$\text{H}_2\text{O}$	. . . . .	26	„

The method of treatment is as follows<sup>1</sup>:—The bauxite is pulverised in disintegrators until it passes through a sieve of  $\frac{1}{4}$ -inch mesh, and is then heated in inclined rotating cylinders at such a temperature that organic matter is burnt off and iron converted into oxide, whilst the solubility of the alumina is unaffected. These cylinders are 33 feet long and 3 feet 3 inches in diameter, and slope at 1 in 25. The ore after passing through these, is cooled by air in a cylinder 30 feet long and 2 feet 6 inches in diameter, with the same inclination as the last one.

The construction of the calcining and cooling cylinders will be clear from Fig. 524. The cooled material is transported by a screw

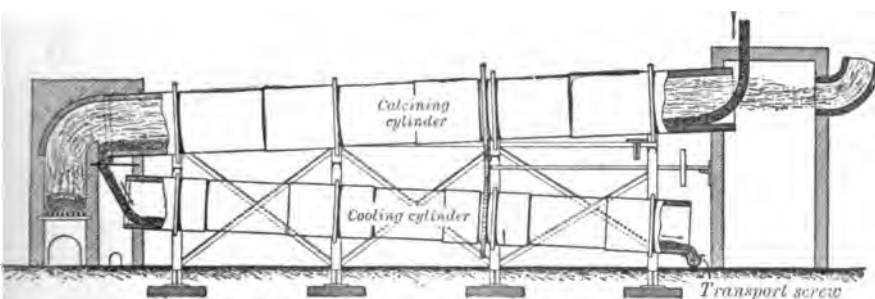
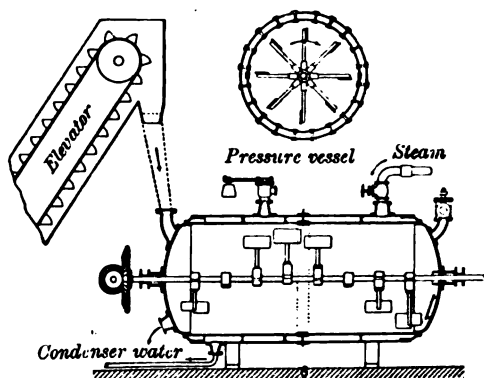


FIG. 524.

to the disintegrator, crushed again to pass through a sieve with 22 meshes to the square inch, and then digested with soda lye of density 1.45 at a pressure of 5 atmospheres in iron pressure vessels 5 feet in diameter, 11 feet 6 inches long, and 0.6 inch thick. These are heated by steam which is first blown into a jacket surrounding the vessel, and then into the inside of the vessel itself. The latter is

<sup>1</sup> *Engineering*, 1896, 62, 291. Borchers, *Elektrometallurgie*, p. 152. Winteler, *Die Aluminium Industrie*, p. 28.

fitted with agitators. The arrangement of the pressure vessel is seen in Figs. 525 and 526. After the charge of 3 tons of material has been agitated 2 or 3 hours it is forced by its own steam pressure into elevated tanks where it is diluted until its specific gravity is 1.23, and then put through a filter press. The filtrate of sodium



FIGS. 525 and 526.

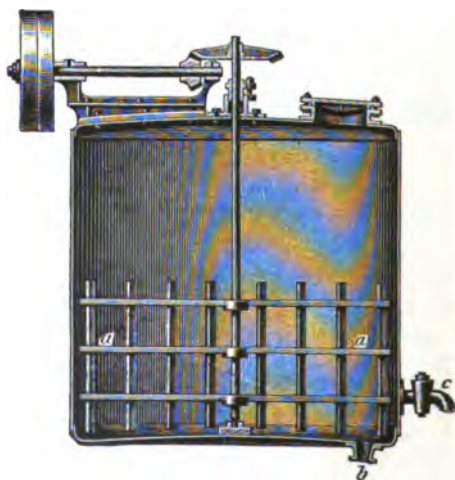


FIG. 527.

aluminate solution is filtered again to clear it completely. The filters are lead-lined boxes each containing 2 sieves of  $\frac{1}{8}$ -inch mesh, covered with pulp obtained by boiling cellulose with water until it forms a thin pap.

The clear solution is now agitated for 36 hours with aluminium hydroxide in cylindrical sheet-iron vessels 20 feet high and 13 feet in diameter. The arrangement is shown in Fig. 527. By this

treatment 70 per cent. of the alumina in solution is precipitated as hydroxide. After this has settled, the clear liquor is drawn off and the precipitate is filtered and washed in a press at 5 atmospheres pressure. The cakes of the hydroxide thus obtained are converted into alumina by heating in an inclined rotating cylinder lined with magnesia and heated with producer gas. Although aluminium hydroxide loses its water at a comparatively low temperature, it is necessary to heat it to bright redness ( $1100^{\circ}\text{C.}$ ), otherwise the alumina absorbs water from the air.

The clear liquor drawn off from the aluminium hydroxide is concentrated in vacuum pans until its specific gravity rises to 1.45. It is then used again in the process. The wash waters from the filter press serve for dissolving caustic soda, and for diluting sodium aluminate solutions.

The plan of the plant at Larne Harbour is given in Fig. 528.

Only a little alumina escapes solution when finely powdered bauxite containing a little silica is treated. It combines with some dissolved silica and an equivalent of soda to form the insoluble compound  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, \text{SiO}_2 + 9\text{H}_2\text{O}$ . Red French bauxite containing 61 per cent. of alumina, and 3 per cent. of silica yields, according to Bayer, 59 per cent. of alumina, i.e. 95 per cent. of its total contents, when the quantities of lye and bauxite

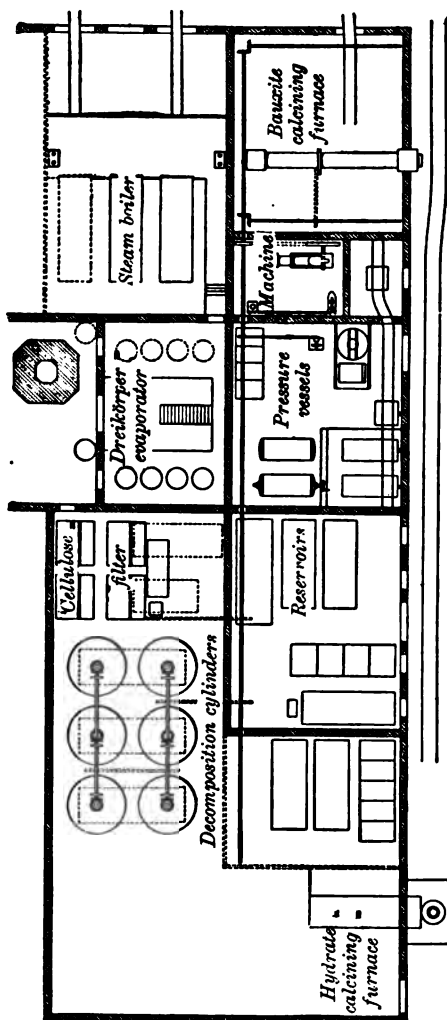


FIG. 528.

are so selected that the ratio of  $\text{Al}_2\text{O}_3$  to  $\text{Na}_2\text{O}$  in solution is as 1 to 1.75 or 1.85. It was mentioned above that 70 per cent. of dissolved alumina is precipitated by agitating sodium aluminate solution with aluminium hydroxide. The ratio of  $\text{Al}_2\text{O}_3$  to  $\text{Na}_2\text{O}$  in solution in this case is as 1 : 6 or 1 : 8.

According to Bayer, when 880 gallons of sodium aluminate containing 4340 grains of  $\text{Al}_2\text{O}_3$  and 4950 grains of  $\text{Na}_2\text{O}$  per gallon (*i.e.* about 6 and 7 per cent. respectively) were agitated with aluminium hydrate, the quantity of alumina remaining in solution varied with the time as follows :—

Period of agitation. Hours.	Quantity of alumina in solution. Grains per gallon.
12	3458
24	2785
36	2380
48	2030
72	1660
84	1246

The ratio of alumina to soda ( $\text{Na}_2\text{O}$ ) in solution at the end of this time was 1 : 5.87.

It has been proposed to extract alumina from bauxite through the sulphate. The bauxite is to be dehydrated by heating in reverberatory furnaces (rotating cylinders), then extracted with sulphuric acid, the sulphate freed from iron evaporated in reverberatories and the residue ignited to drive off sulphuric acid.<sup>1</sup> Pipe-clay or kaolin may be used instead of bauxite. The material in any case must be as free as possible from iron, lime, and magnesia.

At St. Helens<sup>2</sup> the solution vessels are lead-lined tanks, in which 300 gallons of sulphuric acid of specific gravity 1.72, are heated nearly to boiling by live steam, the density being reduced thereby to 1.45—1.475. Into this acid 3,000 lb. of white powdered bauxite are introduced. After charging-in one-third of this quantity the mixture swells up, occupying 6 to 8 times its original volume. The remainder is added slowly, or cold water is run in to prevent this intumescence. The sintering of the mass indicates the end of the reaction. Steam is passed in half an hour longer, and the mixture is then diluted with first hot, then cold, water until the specific gravity is 1.2.

Iron is removed from solution by oxidation with bleaching

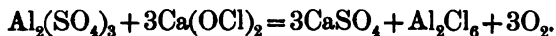
<sup>1</sup> Moissonier, *L'Aluminium*, p. 65. Paris, 1903.

<sup>2</sup> Winteler, *op. cit.*, p. 34.

powder and precipitation with potassium ferrocyanide, or by precipitation with calcium sulphide, or it may be dissolved out before treatment with sulphuric acid, by the action of oxalic acid. The oxalate solution is precipitated with lime and the acid regenerated from the calcium oxalate by means of sulphuric acid.

The iron-free solution of aluminium sulphate is concentrated to 50° B. in vacuum pans, and then taken to dryness in muffles or in gas-fired reverberatories. The solid sulphate is ignited and yields dioxide and trioxide of sulphur, and a residue of friable white alumina which is not hygroscopic and can be straightway electrolysed.

Rothberg<sup>1</sup> has suggested treating the aluminium sulphate obtained from clay and sulphuric acid with chloride of lime, thus:—



The solution of aluminium chloride thus obtained may be precipitated with lime, and the aluminium hydroxide worked up in the usual way. Nothing is known of the application of this suggestion.

Alumina suitable for electrolysis should have the composition:—

$\text{Al}_2\text{O}_3$	. . . .	98	per cent. (minimum)
$\text{SiO}_2$	. . . .	0.3	„ (maximum)
$\text{Fe}_2\text{O}_3$	. . . .	0.1	„ „
$\text{H}_2\text{O}$	. . . .	1.0	„ „

If the cryolite, which must be screened at the mine, is pure, it can be used directly as solvent for alumina; if impure the foreign bodies are precipitated in melting and electrolysing. It can be prepared artificially by dissolving alumina in the equivalent quantity of acid sodium fluoride, NaF, HF, obtained from caustic soda and hydrofluoric acid; or by adding sodium chloride to acid aluminium fluoride in the proportion of 3 mols. of sodium chloride to 1 mol. of alumina, or by treating a mixture of aluminium hydroxide and sodium chloride with the corresponding amount of hydrofluoric acid. Loss of fluorine in electrolysis is best made up by addition of aluminium fluoride. If cryolite be used for this purpose, an excess of sodium salts accumulates in the bath.

The salt suitable for electrolysis is basic aluminium fluoride  $\text{AlOF}$ . This is prepared by neutralising hydrofluoric acid with alumina, the operation being performed by constant stirring in lead-lined wooden vats. The product is dried and calcined at a low

<sup>1</sup> U.S. Pat., 1900, No. 657453. •

temperature. Other methods of preparation will be given later in the description of Grabau's process.

In the technical production of aluminium<sup>1</sup> the cryolite bath is prepared by melting down enough cryolite to cover the bottom of the bath, the heat being supplied by forming an electric arc between anode and cathode. More cryolite is fed in, the anode being gradually moved away from the cathode at the same time. When the anode, which now dips in the molten mineral, has been removed an inch or two away from the cathode, then alumina is added as the aluminium becomes liberated. The metal is tapped occasionally. Cryolite is specifically heavier than aluminium when both are in the solid state, the specific gravities being cryolite=3, solid aluminium=2.7, liquid aluminium=2.54, but in the liquid state the specific gravity of cryolite=2.08, of cryolite saturated with alumina=2.35, of cryolite and aluminium fluoride in the proportion  $\text{Al}_2\text{F}_6.6\text{NaF} : 2\text{Al}_2\text{F}_6 = 1.97$ .<sup>2</sup> Thus molten aluminium is heavier than molten cryolite, and it settles to the bottom of the bath when liberated.

The temperature of the bath is given as 750° C. by Borchers; the decomposition tension of alumina is:

$$\frac{w}{n. 0.24. 96,537} = 2.8 \text{ volts.}$$

Formerly the baths employed were rich in alumina, a much higher temperature was maintained than at present and the tension was 9 to 10 volts, the current density 20,000 to 21,000 ampères per square yard. Now, the temperature is 750° C., the tension 7.5 volts, and the current density 6,000 ampères per square yard of horizontal bath-section, when the horizontal section of molten material is 2 feet 6 inches by 5 feet.<sup>3</sup> With an efficiency of 0.90, the consumption of energy in the production of 1 ton of aluminium per 24 hours is at least 1,400 H.P. Other authorities give 1,400 to 1,600 H.P.

According to Winteler<sup>4</sup> it is advisable to heat by resistance, using short round carbons heated to whiteness by the current, in order to melt down the electrolyte. These carbon rods should be 3 inches long and 1 inch in diameter, for an anode tension of 10 volts and current strength of 400 to 500 ampères. They are arranged at the bottom of the bath so that each rod corresponds to a carbon anode. If the anodes be now brought in contact with these rods the circuit is closed and the heat generated melts the mixed cryolite and

<sup>1</sup> Borchers, *Elektrometallurgie*, 1902, pp. 144-155.

<sup>2</sup> Richards, *Aluminium, Its History*.

<sup>3</sup> Borchers, *op. cit.*, p. 154. Wallace, *Jour. Soc. Chem. Ind.*, 1898, p. 306.

<sup>4</sup> *Op. cit.*, p. 74.



alumina heaped about the electrodes. In this way 220 lbs. of electrolyte can be melted down in 5 to 6 hours with a current strength of 3,200 ampères and a tension of 10 volts. As soon as the bath is half filled with the melt, the anodes are raised, the carbon rods taken out with iron tongs, and the anodes then let down until about  $2\frac{1}{2}$  inches from the bottom. This distance must be kept constant during the electrolysis, which now begins. The aluminium which separates out forms the cathode in place of the carbon, as soon as the metal covers the bottom of the bath.

The composition of the electrolyte must be kept uniform by the occasional addition of alumina, cryolite and aluminium fluoride. The best mixture according to Winteler contains 9 of cryolite to 1 of alumina; this melts at  $940^{\circ}$  C. The melting point can be lowered, if wished, by the addition of common salt. Aluminium fluoride is added to replace the fluorine. It is more suitable than cryolite for this purpose since the latter causes too great a concentration of sodium fluoride in the electrolyte, which becomes worthless in consequence. The electrolyte should appear of a cherry red colour and it should be mobile. The surface should be covered with a crust an inch thick. This is broken through in charging, ladling out aluminium, and regulating the electrodes. The aluminium is best removed every two days in iron ladles; these must not become too hot, otherwise some iron will be absorbed by the molten metal. The aluminium is cast in iron moulds and is remelted.

The depth of the electrolyte should ordinarily be 6 inches when the baths are 12 inches high. If the electrolyte be deeper than this, the electrodes lose some carbon. The tension amounts to 7 to 8 volts, the current density 25,000 to 48,000 ampères per square yard of electrode section.

The following working results are given by Winteler<sup>1</sup> of an experimental trial on a large scale. The average current was 3,160 ampères at 8.5 volts.

The original charge was 220 lbs. of cryolite and 22 lbs. of alumina. This was melted thermo-electrically in 5 hours with the consumption of 203 kilowatt-hours. During the electrolysis the charges were 88 lbs. of cryolite and 75 lbs. of alumina in the first 24 hours, the same quantities in the second 24 hours, in the third 44 lbs. of cryolite and 48 lbs. of alumina; *i.e.* in the first 72 hours 220 lbs. of cryolite and 200 lbs. of alumina. In 10 days and 10 hours the amount introduced was 635 lbs. of cryolite, 590 lbs. of alumina, and 140 lbs. of aluminium fluoride. After 62 hours, 57 lbs.

<sup>1</sup> *Op. cit.*, p. 84.

of aluminium were ladled out, after 86 hours 70 lbs. and so on, the total quantity obtained in the full time being 314 lbs., a layer about 1 inch thick remaining in the bottom of the bath. Including this, the total yield was 417 lbs. of aluminium. The total consumption of electrical energy was 6,716 kilowatt-hours, which corresponds to an output of 608 lbs. of aluminium. Thus the yield was 68.6 per cent. of the theoretical. The aluminium produced contained:—

Al . . . . .	98.4 per cent.
Fe . . . . .	0.9 „
Si . . . . .	0.3 „

Aluminium produced at different times and cast in iron moulds is not of uniform purity. As some of the electrolyte is mixed with the metal when the latter is cast, the ingots must be remelted. They are selected and mixed so that an average metal shall result on melting. The melting is done in graphite crucibles, as free as possible from iron and silicon, otherwise some of these elements will be dissolved by the metal. The temperature must not greatly exceed the melting point of aluminium, since the metal oxidises on strongly heating, and the oxide mixes with the metal to form a pulpy mass. If the temperature be kept well within bounds, the losses on melting do not exceed 3 per cent. The metal contracts by 1.8 per cent. in solidifying, so that the surface of the cast metal is depressed.<sup>1</sup>

The cost of production, etc., for a plant consuming 2,000 kilowatts per 24 hours and producing 1,330 kilos. of aluminium in the same time, and having a supply of cheap water power, is given by Winteler as follows<sup>2</sup> (1 kilo (kg.) = 2.2 lbs.; 1 mark = 1 shilling):—

*Expenditure.*

Pure alumina	3,000 kg, at 38 marks per 100 kg = 1,140 marks.	
Cryolite	300 „ 55 „ „	165 „
Aluminium fluoride	300 „ 40 „ „	120 „
Electrode carbon	1,500 „ 40 „ „	450 „
Current; yearly cost per kilowatt 50 marks		274 „
Wages		150 „
Heating and lighting		10 „
Repairs and new apparatus		50 „
Interest on plant and working capital		50 „
General costs		40 „
Duty and insurance		20 „
Amortisation		50 „
Total		2,519

<sup>1</sup> Winteler, *op. cit.*, p. 88.

<sup>2</sup> *Ibid.*, p. 90.

Receipts: 1,330 kg. of aluminium at 2·2 marks per kilo. = 2,926 marks.

Daily expenditure	2,519 marks
Daily receipts	2,926 „
Cost of 100 kg. aluminium	188 „

Hérault's process is in use at the following places, at all of which water power is used (part of the power at Lend is employed for other purposes): At the works of the Aluminium Industrie Co. at Neuhausen in Switzerland (4,500 H.P.); at Rheinfelden, in Baden (5,040 H.P.); at Lend, near Gastein, Austria (7,500 H.P.); at the works of the Société Electro-metallurgique Française, Froges, Isère; at La Praz, in the Savoy; and at the works of the British Aluminium Co., Foyers, Scotland.<sup>1</sup>

Charles Hall's<sup>2</sup> process consists in subjecting a solution of alumina in molten cryolite to electrolysis, salts of alkalies and alkali earths being added to increase the fusibility. The contents of the various letters patent<sup>3</sup> have undergone an exhaustive criticism by Borchers.<sup>4</sup> The process has been adopted by the Pittsburg Reduction Company, and at Saint Michel de Maurienne in France.<sup>5</sup> Instead of the externally heated baths proposed, those described above heated only by the current are employed.<sup>6</sup> Six gallons of flux are required to dissolve the alumina necessary to yield one pound of aluminium per hour. The tension is 5 to 10 volts.

Joseph B. Hall<sup>7</sup> electrolyses alumina in a bath of aluminium chloride with sodium and lithium chlorides. The electrolyte is supplied by the anode, which consists of a mixture of alumina and charcoal. When the circuit is closed the alumina in the anode passes gradually into the liquid and is there decomposed. The oxygen set free seems to oxidise the carbon of the anode to monoxide. The cell is a vessel made of carbon or a mixture of alumina and carbon with an outer shell of iron: the separated metal collects on the bottom and can be removed from time to time by tapping. The replenishment of bath with alumina by means of anodes of clay and carbon has already been proposed by St. Claire-Deville<sup>8</sup> but has been proved to be unsatisfactory. The process has not been adopted on a large scale.

<sup>1</sup> Borchers, *op. cit.*, p. 157. Minet, *op. cit.* p. 69. <sup>2</sup> *Mineral Industry*, 1893, p. 7.

<sup>3</sup> American Patents. Nos. 400766, 400664, April 2, 1889, and Nos. 400665, 400666, 400667.

<sup>4</sup> *Elektrometallurgie*, p. 131.

<sup>5</sup> Minet, *op. cit.*, p. 71.

<sup>6</sup> *Le Génie civil*, 1898, p. 81.

<sup>7</sup> *Eng. and Min. Journ.*, 1895, p. 581.

<sup>8</sup> *De l'Aluminium*, p. 95. Paris, 1866.

Minet<sup>1</sup> uses an electrolyte of the formula  $12\text{NaCl} + \text{Al}_2\text{F}_6\cdot 6\text{NaF}$  which melts at  $675^\circ\text{C}$ ., has a density of 1.76 at  $829^\circ\text{C}$ ., and begins to volatilise at  $1056^\circ\text{C}$ . At  $800^\circ\text{C}$ . it is fluid enough for electrolysis. In the process aluminium fluoride is decomposed into its constituents, and the loss of aluminium is made good by addition of aluminium fluoride or alumina to the bath. Loss by volatilisation is compensated for by addition of the double salt forming the electrolyte.

He is of the opinion that the fluoride is the real electrolyte, and that the fluorine set free acts upon alumina to form more of this salt, so that the liquid remains unaltered. The baths first used were heated from the outside, the later ones only by the electric current itself.

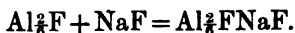
This method, as given in the letters patent<sup>2</sup> has been exhaustively criticised by Borchers.<sup>3</sup> It was first introduced in Paris (impasse du Moulin-Joli) in 1887, and in 1888 in Creil, Department of Oise. In 1891 a plant was transferred to Saint Michel de Maurienne where it was kept going by water power (500 H.P.) until 1894.<sup>4</sup> The method is no longer used now.

#### B. Preparation of Aluminium by Electrolysis of Aluminium Fluoride.

To this category belongs Minet's process, viz. the electrolysis of the mixture,  $\text{Al}_2\text{F}_6\cdot 6\text{NaF} + 12\text{NaCl}$  aluminium fluoride being added to the bath during the operation. The equation representing the electrolytic decomposition is:—



If the loss of aluminium were made good by addition of cryolite, the bath would become too rich in sodium fluoride, so that sodium would soon be liberated instead of aluminium. Therefore aluminium fluoride is employed, and this combines with the sodium fluoride thus:—



This process has been tried experimentally at the works where Minet's other process (the electrolysis of alumina) is in operation. the same apparatus being used. The following data for some of

<sup>1</sup> *Op. cit.*, p. 48.

<sup>2</sup> Eng. Pat. No. 10057, 1887.

<sup>3</sup> *Elektrometallurgie*, 1902, p. 137.

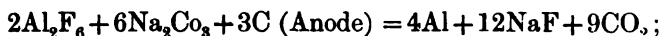
<sup>4</sup> Minet, *op. cit.*, p. 47.

the more important compounds employed have been calculated by Minet<sup>1</sup> :—

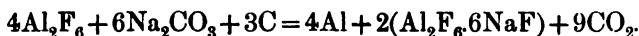
Compound.	Tension of decomposition.	Heat of combination.
Aluminium fluoride . . . .	3·04 volts. . . .	70·0 cal.
Sodium chloride . . . .	4·23 „ . . . .	97·3 „
Sodium fluoride . . . .	4·82 „ . . . .	110·8 „

Grabau<sup>2</sup> subjects to electrolysis a fused mixture of the fluoride (or oxyfluoride) with soda or potash and obtains besides aluminium an alkali fluoride, or else cryolite. The fusion and electrolysis are performed by the aid of the electric arc. Cryolite is first fused in the vessel, and then a mixture of aluminium fluoride and soda introduced. The anode is carbon, the cathode a metal, preferably aluminium. During electrolysis the metal separates at the cathode and carbon dioxide is set free at the anode. This comes partly from the molten material oxidising the anode, and partly from the action of the aluminium fluoride on the soda. Instead of the fluoride, the oxyfluoride is sometimes used, which is easily prepared.

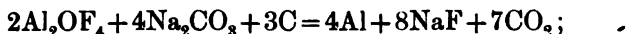
The proportion in which either of these is mixed with the alkali carbonate depends upon whether sodium fluoride or cryolite is desired as a by-product. When the fluoride is employed, and sodium fluoride is formed, the action is as follows :—



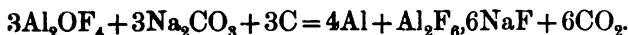
but if cryolite is to be the by-product the action must be :—



When the oxyfluoride is used, and sodium fluoride is to be the secondary product, the action should be according to the equation :—



while to give cryolite the action should be :—



Borchers<sup>3</sup> considers it probable that the lively evolution of carbonic acid noticed when the mixture of aluminium fluorides and alkaline carbonates is fused, takes place according to this equation :—



According to this the electrolyte is oxide of aluminium dissolved in alkali fluorides.

<sup>1</sup> *Op. cit.*, p. 49.

<sup>2</sup> Ger. Pat., No. 62851, 1891.

<sup>3</sup> *Elektrometallurgie*, p. 148.

The advantages of this process are the purity of the aluminium, as the material is easily prepared free from iron and silica, and the production of cryolite as a by-product. Nothing is known of the application of this process.

To obtain pure aluminium fluoride, which is absolutely necessary for pure aluminium, as well as to obtain it merely free from iron. Grabau has devised special processes.

To make the pure compound,<sup>1</sup> powdered calcined clay, as free as possible from iron, is taken, and treated in slight excess with hydrofluoric acid of 12 per cent. strength, or with correspondingly stronger hydrofluosilicic acid. When hydrofluoric acid is used, the temperature must be kept down to 95°; but if the other acid is used, the action must be assisted by heating.

The mass becomes neutral in a few minutes, after which the liquid, consisting of aluminium fluoride, is filtered at a medium temperature from the residue, which is hydrated silica and undecomposed clay. The residue is washed with hot water, which removes any aluminium fluoride remaining. In this way 90 per cent. of the hydrofluoric acid added seems to be used to form the aluminium fluoride.<sup>2</sup>

To obtain this fluoride merely free from iron,<sup>3</sup> a solution of it is treated first with sulphuretted hydrogen to remove lead, arsenic, and other metals, and to reduce ferric salts present to ferrous. This reduction is necessary, as otherwise ferric fluoride is found in the crystals of aluminium fluoride obtained. The liquid, filtered from the residue, is acidified to prevent the precipitation of traces of iron sulphide in the cooling which follows, and then cooled in vessels made of sheet aluminium. Here hydrated crystals of aluminium fluoride separate out ( $\text{Al}_2\text{F}_6 \cdot 18\text{H}_2\text{O}$ ). The crystallisation is concluded as soon as the temperature, which rose at the beginning, has been brought down to 0° by continued cooling. The whole is separated into mother liquor and crystals in centrifugal pans, and the crystals are washed with ice-cold water.

### C. *Preparation of Aluminium by Electrolysis of Aluminium Sulphide.*

The preparation of the metal from its sulphide has been proposed by Bucherer in Cleveland, and also by the Aluminium-Industrie-Actien-Gesellschaft in Neuhausen.

<sup>1</sup> Ger. Pat., No. 69791.

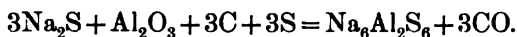
<sup>2</sup> Ger. Pat., No. 70155.

<sup>3</sup> *Zeitschr. für angew. Chem.*, 1893, p. 462.

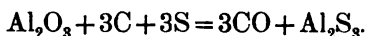
Bucherer, in Cleveland, Ohio, U.S.A.,<sup>1</sup> uses aluminium sulphide in the form of double sulphide with an alkali or alkali earth.

This is subjected to electrolysis in a bath of molten chloride or fluoride of alkali or alkali earth, or of a mixture of them. Sodium or potassium chloride, or the two mixed, is found to be the best solvent. The double sulphide is made more cheaply and easily than aluminium sulphide alone, and yields a pure metal when electrolysed, aluminium being separated at the cathode by a current of low potential.

The double sulphide is prepared by Bucherer, by heating aluminium oxide or hydrate with the sulphide or polysulphide of an alkali or alkali earth, and excess of sulphur and coal. The action is as follows:—



He proposes to make pure aluminium sulphide by the slow action of sulphur vapour on a mixture of alumina and carbon heated to white heat in a clay retort. The action would then be:—



The process of the Aluminium-Industrie Co., in Neuhausen,<sup>2</sup> consists in electrolysing the sulphide  $\text{Al}_2\text{S}_3$  alone or in a bath of an alkali or alkali-earthly chloride, or fluoride. The electrolyte may be fused and maintained liquid with the help of external heat, or by the current alone. If the solution of aluminium sulphide in sodium or potassium chloride is first fused in a vessel heated from without, and then kept fluid during the electrolysis, a current with a potential of 2·5 to 3 volts will be enough to electrolyse the sulphide; but if the solution is fused and kept fluid by the current alone, a potential of 5 volts will be necessary.

The process seems to be best carried on in a vessel of cast or wrought iron, which is lined with charcoal. Aluminium appears at the cathode, sulphur at the anode. The liquid itself generally prevents the oxidation of the sulphide; if it is desired to secure this further, reducing gases are passed over the fused mass.

In this process the lining of the vessel is not attacked, nor the carbon electrodes dipping into the molten electrolyte, because the temperature of the bath is not high enough for the sulphur set free to combine with carbon. Consequently the aluminium is very pure.

<sup>1</sup> Ger. Pat., No. 63995, November 18, 1890.

<sup>2</sup> Ger. Pat., No. 68909.

Further advantages in the method may be pointed out:—the comparatively small strength of current needed, the prevention of short circuiting, as aluminium is heavier than the liquid, and sinks quickly to the bottom, and the possibility of collecting the sulphur fumes at the anode, and utilising them. The preparation of aluminium sulphide by the methods at present in use is very expensive, for pure alumina must be used, and this itself can be directly electrolysed. Again, treating the alumina, carbon and sulphur to obtain the sulphide, requires a large amount of heat energy. Practical application of the process, therefore, is not likely at present; it can only

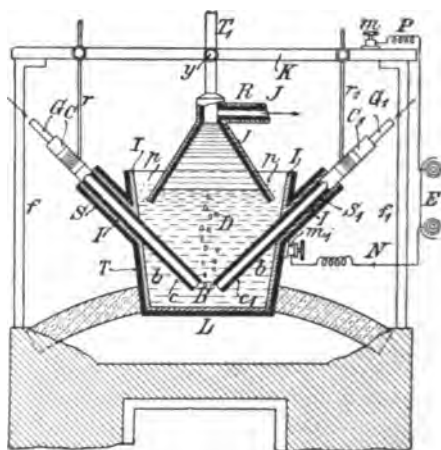


FIG. 529.

become possible after some cheap method of obtaining aluminium sulphide has been invented.

Gooch prepares aluminium sulphide in the bath itself by passing a stream of carbon disulphide into the molten bath of fluoride and chloride of aluminium, alumina being added to compensate for the aluminium separated in the process. The carbon disulphide and the alumina together form aluminium sulphide, from which the metal is liberated by the action of the current.

The apparatus is shown in Fig. 529.  $T$  is the bath lined with carbon.  $CC_1$  the anodes movable in the tubes  $SS_1$ , which are lined with clay. The current enters the anodes through the rods  $rr_1$ , which are in metallic connection with the bar  $K$  and the leads  $P$ . The cathode is formed by the carbon lining of the bath, which is in connection with the leads  $N$ . Carbon disulphide enters the bath through the hollow



anodes and their prolongations  $GG_1$ . A hood  $J$  serves to convey vapours arising from the bath into the surface of the electrolyte lying outside the hood is c of charcoal  $p$  during electrolysis. The aluminium at the bottom of the bath. The apparatus has no large scale.

### 3. PREPARATION OF ALUMINIUM ALLO

The process of Cowles Brothers and that of E on the large scale to prepare the alloys directly u ago. But since we are now able to produce alumin metallurgically in large quantity, these original pro much used, as it is more economical to make the aluminium with the necessary metal.

#### *The Cowles Brothers' Process*<sup>1</sup>

is used in Cleveland, Ohio, U.S.A., and was publish consists in extracting aluminium from a mixture charcoal by an electric current, and alloying this wi the moment it is reduced. The current produces th to reduce aluminium, because of the resistance of alumina and charcoal.

The arrangement of the Cowles apparatus is sho and 531.<sup>2</sup> Fig. 530 is a longitudinal and Fig. 5 section.

The furnace consists of a box of rectangular se and hearth made of fire-clay.  $E, E$ , are the electr bundles of carbon pencils, usually 9, about  $1\frac{1}{4}$  inches placed in metallic cylindrical cases,  $M$ , cast roun consist of iron or copper according to the alloy a head of each case is a copper rod  $K$ , making conr conductor  $L$  through the copper clamp  $V$ , to w on one side the conically pointed end of the cop the other, the end of the wire  $L$ .  $R$  represen cast-iron tubes, in which the electrodes may be m backwards by the screws  $S$ . The carbon pencils a

<sup>1</sup> U.S. Pat., No. 319795.

<sup>2</sup> Borchers, *Elektrometallurgie*, p. 102; *Industries*, vol. cx

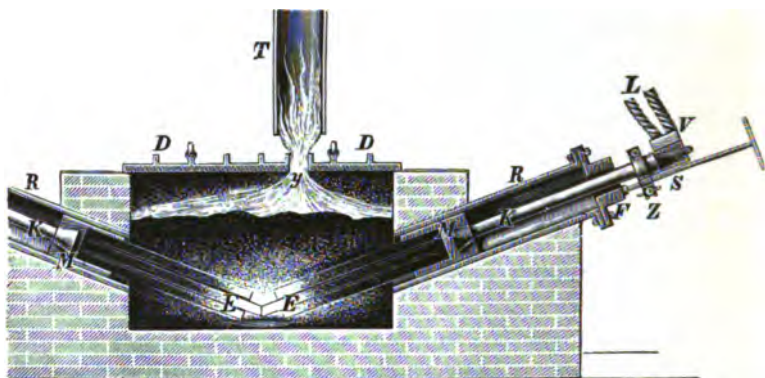


FIG. 530.

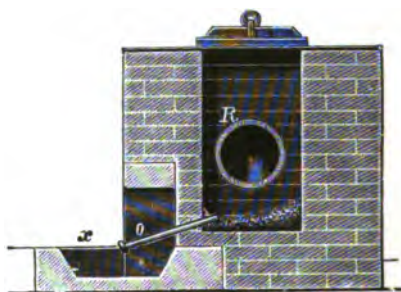


FIG. 531.

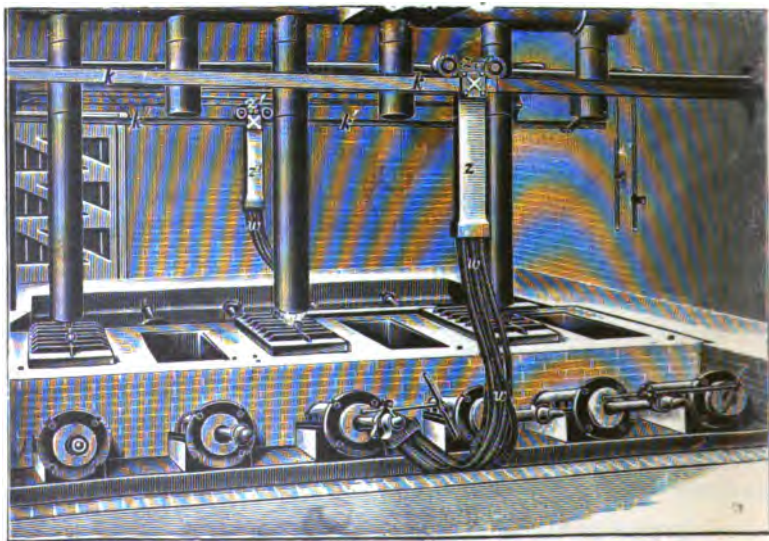


FIG. 532.

to the current, become red-hot, and communicate to charcoal, alumina and metal around them. *D* is apparatus, made of cast iron. The opening *y* in this monoxide gas formed by the oxidation of the charcoal the tube *T*, which is in communication with a condenser arrest any alumina carried off by it. *o* is the tap molten alloy out into the receiver *x*.

A furnace is about 5 feet long; they are built shown in Fig. 532.<sup>1</sup> This shows part of the plant Syndicate Co.," which has now been disused for a current was produced by a Crompton Dynamo Machine it had a potential of 60 volts and a strength of 6,000

The current was conducted by copper wires to *k* and *k'* which ran respectively along the front and back furnaces. The wires were attached to the rods by clamps. The upper ends of these had pulleys which ran on a track. From their lower ends ran bundles of copper wire. At their turn were connected with copper rods in the way shown in figure.

Only one furnace was worked at a time, the other being cooled, charged or emptied. The operation is as follows: First, a layer of wood charcoal to the depth of 2 inches was spread out on the bottom of the furnace. This was soaked in milk of lime and dried to prevent its burning. Then the electrodes were put in place. Next a frame of iron plate is introduced, and the space within it filled with alumina (bauxite, corundum or emery), wood charcoal with which the alloy is to be made. These substances are finely divided. (The metal is sometimes not finely divided, but in rods which are arranged in the furnace either perpendicular to the long axis.) The space between the rods and the side walls of the oven is filled with a lining of carbon, after which the frame is removed. A conductor of carbon through the furnace is then formed by arranging the rods in a circle, and any space remaining is filled with wood charcoal. A cover is next put on, and the current started. The reduction of alumina is indicated by the appearance of a red glow. The aluminium which separates forms an alloy with the metal which has been put in; this collects at the bottom of the furnace, and is tapped out at the end of the operation. At the same time a sort of slag is formed which is an intimate

<sup>1</sup> *Industries, L.C. ; Borchers, L.C., p. 100.*

alloy with charcoal. This is powdered and washed, and the portions containing metal are added to another charge. Carbon monoxide is formed from the oxygen of alumina and the charcoal. It passes through an opening in the cover, and through a condenser as already explained.

The end of the process is known by the cessation of the white smoke. The smelting lasts about one hour. The furnace is thrown out of circuit, and the current at once turned on in another one. The amount of aluminium in the alloy is 15 to 35 per cent. This may be converted into any other percentage by melting it with aluminium or the other metal, or any new metal as desired. So, for example, aluminium bronze is obtained by melting this alloy with copper so that the correct percentage of aluminium is obtained (from 1.25 up to 10 per cent.).

The strength of current and horse-power of the dynamo used by the "Cowles Syndicate Co." have been already stated.

The amount of ferro-aluminium or aluminium bronze turned out daily is 750—1,000 kg. (15—20 cwt.), containing 15 to 17 per cent. aluminium. The expenditure of energy necessary to produce 1 kg. of aluminium has been found to be on the average 50 h.p.<sup>1</sup> As it varies between 53.5 and 25, the lowest average that can be taken is 40 h.p.<sup>2</sup> The theoretical energy needed for 1 kg. of aluminium in bronze is only 8.87 h.p. Thus the waste of energy is very considerable. The reason appears to be that alumina is formed over again. The white smoke seen in the process seems to be newly formed alumina, formed by the reaction of aluminium vapour and carbon monoxide in the cooler part of the furnace.

At the Cowles Brothers' Works at Lockport in the State of New York water-power to the extent of 1,200 h.p. is at their disposal: and from 2 to 3 tons of aluminium bronze are said to be daily produced. The walls of the vessel are lined with wood-charcoal, mixed with chalk, because otherwise the charcoal might be converted into graphite while the current passes, and graphite is a good conductor of heat and electricity.<sup>3</sup>

#### *Hérault's Process.*

In this process alumina is not only fused by an electric current, but decomposed, and the aluminium alloyed with another metal at

<sup>1</sup> Borchers, *Elektrometallurgie*, p. 101.

<sup>2</sup> Dammer, *Chem. Tech.*, vol. ii., p. 222.

<sup>3</sup> Dr. Charles v. Hahn, *Zeitschr. für Elektrotechnik*, 1895, p. 479.

the moment it is set free. The second me  
forms the cathode; the anode is a bundle of c  
fused by the current, forms the electrolyte.  
apparatus were described on p. 810.

The method is used at the works of th  
Actien-Gesellschaft at Neuhausen in Sw  
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